Photoinitiated Polymerization by Phosphonium Salts Incorporating a Chromophore Unit

by

Aal-e-Ali

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

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In

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Aal-e-Ali, M.S.

King Fahd University of Petroleum and Minerals (Saudi Arabia), 1989

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

PHOTOINITIATED POLYMERIZATION BY PHOSPHONIUM SALTS INCORPORATING A CHROMOPHORE UNIT

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This thesis, written by **Aal-e-Ali** under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE.

Thesis Committee

Thesis Advisor (Dr. I. I. Abu-Abdoun)

Member (Dr. Shaikh Asrof Ali)

Member (Dr. Uwe K. A. Klein)

Department Chairman

Dean, College of Graduate Studies

April 26, 1989
Date

Dedicated
to
my parents

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First and foremost thanks to ALLAH, THE ALMIGHTY, who gave me patience and ability to accomplish this work.

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THESIS ABSTRACT

FULL NAME OF STUDENT : AAL-E-ALI

TITLE OF STUDY : PHOTOINITIATED POLYMERIZATION BY PHOSPHONIUM SALTS INCORPORATING A CHROMOPHORE UNIT

MAJOR FIELD : CHEMISTRY

DATE OF DEGREE : APRIL, 1989

Suitable synthetic methods have been developed for the preparation and isolation of phosphonium and arsonium salts containing a specific absorbing functionality in the same molecule. Cationic polymerization of epoxide monomers such as cyclohexeneoxide and vinyl monomers such as p-methylstyrene and styrene and free radical polymerization of methylmethacrylate by these salts has been demonstrated. Experimental results are presented to show the effect of salt counterion, photolysis time, light intensity and the variation of salt concentration on the rate of conversion to poly(cyclohexeneoxide), poly(p-methylstyrene), polystyrene, and poly(methylmethacrylate). Molecular weight of the resulting polymers have been determined in some important cases. The anionic part of these salts determine their efficiency in photoinitiated polymerization and the reactivity order is found to be $SbF_6^- >> PF_6^- >>> BF_4^-$. Salts with BF_4^- anions are completely unreactive in the cationic polymerization system. N-Methylphenothiazine and pyrene are shown to be effective sensitizers in the cyclohexeneoxide polymerization. The reaction mechanism of the sensitization is expected to be single electron transfer with ultimate initiation by the N-methylphenothiazine cation radical. Neither phosphonium nor arsonium ylid of the isolated salts were seen to be effective photoinitiator for cationic polymerization, instead the ylid acted as a terminating species. The cationically initiated species are more likely due to the interaction of the monomer with the photoexcited salts leading to polymer with the salt as end groups. In case of methylmethacrylate polymerization the rate of polymerization was very slow with the phenacylarsonium salt. The proposed mechanism indicates phenyl radical as the potential free radical initiating species. Finally the salts are shown to be effective photoinitiator for epoxide and vinyl polymerization and slightly affected by temperature above 70 °C depending on their chemical structure. This work will contribute to the development of new hybrid photoinitiator systems and the goal of achieving more efficient photoinitiators in the polymerization of mixture of acrylate and epoxy monomers. Also this study yielded data about the nature and reactivities of intermediates and the mechanism of the polymerization of the system involved.

MASTER OF SCIENCE DEGREE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
Dhahran, Saudi arabia

April, 1989

خلاصة الرسالة

اسم الطالب الكامل : آل علي

عنوان الدراسة : تنشيط البلمرة الضوئية باستعمال مركبات أملاح الفسفور المتأثرة بالضوء

التخصص : كيمياء

تاريخ الشهادة : ابريل ١٩٨٩

تناقش هذه الرسالة طرق تحضير واستعمال بعض مركبات أملاح الفسفور والزرنيخ التي تحتوي على مجموعات وظيفية ماصة للضوء وتعمل كمنشطات لتفاعلات البلمرة الكاتونية للمونيمرات التي تحتوي على مجموعة الفينيل والايبوكسي . تناقش النتائج العملية في هذه الرسالة العلمية تأثر عمليات البلمرة بتغيير كل من الشق السالب والموجب ، تركيز الملح ، مدة التفاعل ، كثافة الضوء المستعمل ونوع المونيمر في عملية البلمرة ، ولقد تبين ان زيادة سرعة البلمرة بالاعتماد على الشق السالب تقع ضمن الترتيب التالي : $SbF_6^- > > PF_6^- >>> BF_4^-$ وقد تم معرفة الوزن الجزيئي للبوليمر الناتج في بعض الحالات المهمة . تظهر هذه الدراسة ان سرعة البلمرة تزداد باستعمال مواد ممتصة للضوء مثل البيرين والفيناثيوزين حيث تمتص هذه المركبات الضوء وتنقله للمركب المنشط . ترجح نتائج هذه الدراسة حدوث عملية البلمرة الكاتونية نتيجة تفاعل المنشط في حالته النشطة(Photoexcited state) مع المونيمر في حالة الثبات وفي حالة البلمرة بالشق الجذر فإن تكون مجموعة الفينيل ذات الجذر الحر هي العامل على تنشيط عملية البلمرة .

واخيرا بينت هذه الدراسة انه بالرغم من ثبات هذه المركبات في درجة الحرارة ٣٥° م بعيداً عن الضوء ونشاطها الضوئي إلا انها تعمل على تنشيط تفاعلات البلمرة بدون تعرضها للضوء على درجة حرارة اعلى من ٥٠° م وبمعدل قليل جداً مقارنة مع نشاطها الضوئي . من المؤمل ان يسهم هذا البحث في تطوير مركبات ذات نشاط مزدوج في تفاعلات البلمرة تعمل على تنشيط عملية البلمرة الكاتونية والبلمرة بالجذر الحر بناء على اختيار ظروف التفاعل والمونيمر المستعمل كذلك تسهم نتائج هذا البحث في تكون مبلمرات قد تعمل كمواد مساعدة وذلك لتوفر الملح المستعمل في عملية التنشيط ضمن سلسلة البوليمر المتكونة .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

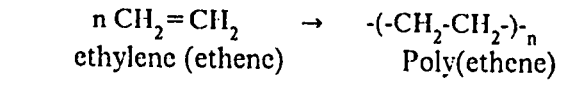
الظهران ، المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

1.1. THE NATURE OF POLYMERIZATION :

Polymers are substances of high relative molecular mass, formed by the covalent linking of small molecules known as monomers. In the process of addition polymerization, the linking occurs through the breaking of bonds and formation of new bonds with other similar units. The monomer generally contains a double bond or a strained ring.



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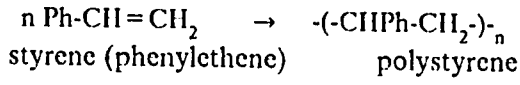

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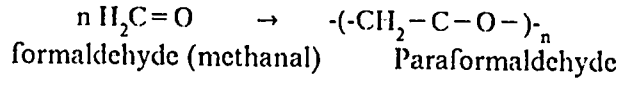

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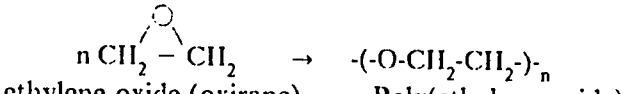

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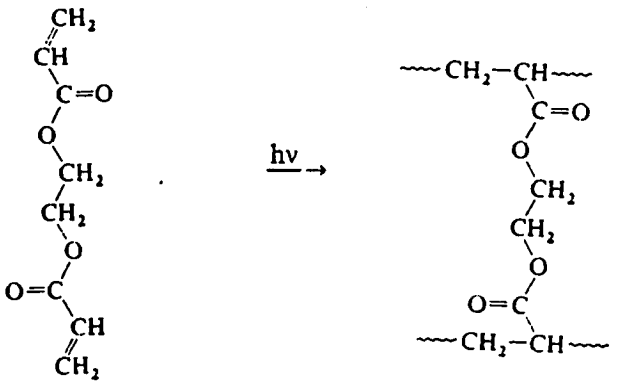
Polymers formed in this way need not be simple linear chains of monomer units joined end to end. Branched polymers may be formed, in which monomer units become attached in such a way that side-chains are formed. Diacrylates and triacylates are examples of monomers used commercially which exploit this to produce tough and durable films. A particular example is the polymerization of ethylene glycol diacrylate (eq-5). Materials of this type are used in laquers and varnishes, which are formed by the effects of light. They are used in coating tin plates, paper and wood.



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ethylene glycol diacrylate

poly(ethylene glycol diacrylate)

The general mechanism of polymerization involves three types of reaction :

1. the formation of reactive intermediates (initiation),
2. the reaction of monomers to form large assemblies (propagation),
3. the disappearance of reactive intermediates (termination).

Such a sequence, which constitute a chain reaction, can be brought about by a radical mechanism. An alternative mechanism for coupling double bonded or cyclic monomers involves the formation of ions, which can grow or terminate in a similar manner to radicals.

Photochemical excitation is an important method of initiation. It has the advantage of operating only whilst the system is exposed to the appropriate radiation. Also it is effective at room temperature, and solvents are generally not necessary; both these factors are of considerable economic and environmental advantage.

1.2. POLYMERIZATION KINETICS :

A proper understanding of the photoinitiation of polymerization can be achieved only through some formalization of the kinetics. The first stage of addition polymerization requires the generation of reactive intermediates

$$\text{initiator} \rightarrow X^{\cdot} \qquad 6$$

Heat or light generates the reactive species, $X^{\cdot}$, which can react with a monomer and begins the sequence of monomer-consuming reactions to form polymer:

$$X^{\cdot} + M \rightarrow XM^{\cdot} \qquad 7$$

$$XM^{\cdot} + M \rightarrow XM_2^{\cdot} \text{ etc.} \qquad 8$$

The sequence can be stopped by one of a number of termination steps. In radical systems, combination and disproportionation are important:

$$XM_m^{\cdot} + XM_n^{\cdot} \rightarrow XM_{m+n}X \text{ (combination)} \qquad 9$$

$$XM_m^{\cdot} + XM_n^{\cdot} \rightarrow XM_m H + XM_n(-H) \text{ (disproportionation)} \qquad 10$$

In ionic systems other termination processes operate.

Rarely does each sequence of reactions form an individual initiating centre from only one polymer molecule, because growing chains have the tendency to transfer 'activity' by reaction with another molecule known as a chain transfer agent, represented here as S :

$$XM_n^{\cdot} + S \rightarrow XM_n + S^{\cdot} \quad 11$$

A chain-transfer agent may be added specifically to the system or it may be solvent, monomer, adventitious impurity, or another polymer molecule. This is followed by the reaction of $S^{\cdot}$ with a monomer molecule

$$S^{\cdot} + M \rightarrow SM^{\cdot} \quad 12$$

and hence no chain propagation centres are lost. Clearly the average relative molecular mass of polymer formed will depend on the transfer efficiencies, as well as on the relative probability of propagation and termination.

The chemical structure of the monomer determines the nature of the reactive site, which may be a radical, an anion or a cation. The cationic mechanism is favoured by monomers with electron repelling substituents, such as alkyl groups, whereas radical and anionic reactions are favoured by electron-withdrawing groups, such as CN and COOR.

Photolytic decomposition of an initiator to form radicals is particularly important. The full polymerization sequence is :

$$\text{initiator} \xrightarrow{h\nu} 2R^{\cdot} \quad 13$$

$$R^{\cdot} + M \rightarrow RM^{\cdot} \quad 14$$

$$RM^{\cdot} + M \rightarrow RM_2^{\cdot} \quad 15$$

$$RM_n^{\cdot} + M \rightarrow RM_{n+1}^{\cdot} \quad 16$$

$$RM_m^{\cdot} + RM_n^{\cdot} \rightarrow RM_{m+n}R \quad 17$$

$$RM_m^{\cdot} + RM_n^{\cdot} \rightarrow RM_mH + RM_n(-H) \quad 18$$

The rate of polymerization is given by

$$\text{rate} = \sum k_p[RM_i][M] \qquad 19$$

where k_p is the rate constant for reaction of a polymer radical with monomer and $\sum[RM_i]$ is the total concentration of polymer radicals. For simplicity, it is assumed that k_p is the same for all propagation steps. The conditions of polymerizations are such that, in reactions of this type, polymer formation proceeds steadily at a rate that decreases because of the fall in the concentration of the reactive monomer, and the concentration of chain-propagating centres is effectively invarrient during irradiation:

$$d(\sum[RM_i])/dt = \text{initiation rate - termination rate} = 0 \qquad 20$$

So we can write

$$\Phi_R I_{abs} - k_t(\sum[RM_i])^2 = 0 \qquad 21$$

and hence

$$\sum[RM_i] = (\Phi_R I_{abs}/k_t)^{1/2} \qquad 22$$

where I_{abs} is the intensity of light absorbed by the initiator, Φ_R is the quantum yield of radical produced by its decomposition, and k_t is the rate constant for radical termination. Hence the rate of polymerization is given by

$$\text{rate} = k_p[M](\Phi_R I_{abs}/k_t)^{1/2} \qquad 23$$

It is important to note that the dependence of the rate on the root squire of the intensity of the absorbed light is a consequence of the bimolecular termination reactions that occurs in radical systems.

If the intensity of light absorbed is increased, the concentration of propagating radicals is greater and consequently the rate of termination is inhanced. This has the

effect of reducing the average relative molecular mass of the polymer molecules produced.

Although the most usual consequence of photoactivation of a molecule in the 250-400 nm region is the generation of neutral radical centres by bond homolysis, reactive ions can be generated either directly or indirectly in many systems. This allows a wider variety of monomers to be selectively polymerized. An additional advantage of ionic system is that the troublesome effects of oxygen, which interferes with radical polymerization, can be avoided.

In ionic polymerization, termination is not due to interaction between two growing polymer molecules, owing in part to the strong electrostatic repulsion between like charges, and the rate is usually dependant on I_{abs} rather than $(I_{abs})^{1/2}$ This means that more effective polymerization can be achieved with intense light sources when ionic initiators are used.

In ionic polymerization systems the termination processes are inefficient, and the polymerization may continue for a considerable time after irradiation has ceased. This is very useful in pigmented systems used in lacquers and inks, where opaque particles, such as those of titanium dioxide, which may be present in commercial preparations, prevent illumination of the whole volume of the system. Diffusion of the reaction centres through the systems can overcome this problem if they are sufficiently long-lived.

1.3. PHOTOINITIATED POLYMERIZATION :

Photoinitiated polymerization has been the subject of intense scientific and industrial activity during the past two decades, as the application of this technology

multiplied in surface coatings, photography and printing plates. A photoinitiator is a compound added to facilitate the initiation of a reaction when a reaction mixture is irradiated with a suitable wavelength. This additive may absorb actinic radiation and break to form the primary reactive species free radical, cation or cation radical. An additive may function as a sensitizer in a strictest sense, that is, absorb then transfer energy to another molecule that forms a primary reactive species. In this type of energy-transfer mechanism, the sensitizer is not consumed or structurally altered. A sensitizer may be defined as compound having a positive influence on the photochemical reaction rate as described above, and in this sense, the photosensitizer may therefore be regarded as a photocatalyst. The additive may also be excited to a state with unpaired electrons, i.e. triplet state, which may accept or donate electron from or to another molecule which now having an unpaired electron, acts as the reactive species in subsequent steps. The additive may also form a readily excited complex which may then undergo fission to form reactive species. There are also compounds which may be termed photo-optical sensitizers. These give a red shift to polymers, they extend their optical sensitivity to radiation of a longer wave length.

1.4. LIGHT ABSORPTION AND EXCITED STATE MECHANISM :-

The most important step in any photochemical reaction is the absorption of light energy, emitted from a given source, by the reacting molecule (in our case photosensitizer or photoinitiator as the absorbing species).

For this reason it is important to select photosensitizers and photoinitiators with absorption bands that overlap the emission spectra of the various commercial UV-curing light source (only the light absorbed by a molecule evokes photochemical reactions). Absorption by any organic molecule is governed by the arrangement of

atoms in the molecule.

The basic ultraviolet absorption spectrum of photosensitizers or photoinitiators involve electronic transitions between π (bonding) and π^* (antibonding) molecular orbitals characteristic of aromatic molecules as well as n (non-bonding) to π^* transitions associated with various carbonyl compounds (Fig.1.1). The probability of transition is measured or related to an experimental absorption coefficient or extinction coefficient (ε). Large value of ε indicates a high probability of absorption by a molecule at a given wavelength and low values of ε represent less probability of absorption.[1-8]

After absorption of energy the excited photosensitive molecules can undergo various types of photophysical deactivation pathways (Fig.1.2). Most excited state chemical reactions occur form the triplet excited state of the photosensitizer or photoinitiator. If the triplet lifetime of the photoinitiator is short then the chance of reaction or formation of an active intermediate initiator species is less. If the triplet lifetimes are long then the chance of undergoing reaction is greater.[9,10]

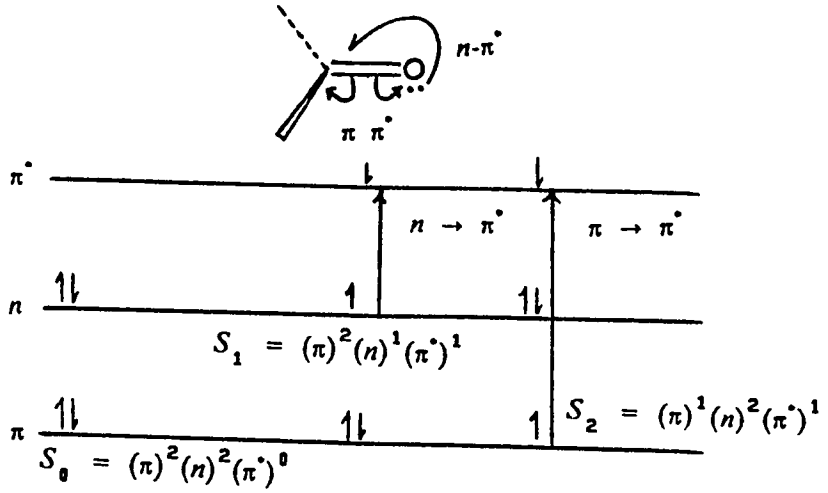
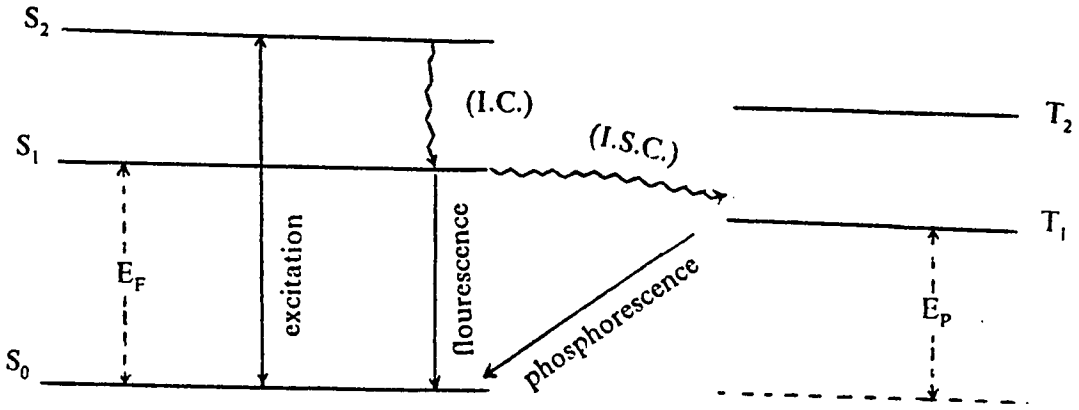


Figure 1.1 : Electronic transition of carbonyl compounds (ref.[1c])



S_0 = ground state
S_2 = upper singlet level
S_1 = lower singlet level
E_F = Energy of lower singlet level
T_1 = lower triplet level
T_2 = upper triplet level
E_P = Energy of lowest triplet state
I.C. = radiationless internal conversion process
I.S.C. = radiationless inter-system crossing process

Figure 1.2 : Jablonski diagram. (ref.[1c])

Photochemical production of active intermediates from the excited singlet state organic molecule compete with the rate of intersystem crossing (excited singlet to excited triplet state); and the rate of production of active intermediates from the triplet excited state compete with the triplet-state decay.

The next major section of the photocuring process is the effect of the various photoinitiators on the rates of photopolymerization. In general, there are four major types of photoinitiators :

1. Those that undergo direct photofragmentation upon exposure to light irradiation and produce free radical or Lewis acid reactive intermediates.
2. Those that undergo electron transfer reaction followed by rearrangement into a free radical species.
3. Combinations of photosensitizers with photoinitiators through energy transfer mechanisms.
4. Hydrogen absorption reactions to produce free radical intermediates.

1.5. EFFICIENCY OF PHOTOINITIATION

The overall efficiency of photoinitiation is the product of the efficiencies at each stage of the process, including absorption, intersystem crossing, initiator or reactive intermediate (e.g. radical, cation or cation-radical) formation and initiation. Thus overall efficiency is the product of (1) the incident light which is absorbed by the photoinitiator or the photosensitizer, (2) the fraction of excited state singlet which are transformed into triplet, (3) the fraction of triplet which yields initiator radicals, and (4) the fraction of reactive intermediate which initiate polymerization. It is known that major competing processes are

(a) singlet and triplet decay.

(b) Triplet quenching by O_2, monomer and ground state photoinitiator.

(c) Initiator radical recombination as well as reaction of initiator radical with O_2. The reaction of initiator radical and O_2 with growing polymer chains also adversly affect the film property in U.V. curing.

1.6. PROPERTIES OF PHOTOINITIATORS

The most important properties of a compound that is to be used as photoinitiator are as follows :

1. The initiator should be stable under all reasonable conditions, except the irradiation conditions to be used.
2. The absorption of the initiator should be such that the photochemical reaction arising from normal room lighting conditions is insignificant; the maximum absorption coincides as nearly as possible with the most intense emissions from available light sources; the colour of the initiator or the products derived therefrom does not interfere with the appearance and other properties of the polymer products; the absorption overlaps as little as possible with those of the monomer and added pigments.
3. The quantum yield of formation of reactive intermediates from the initiators should be as high as possible. This yield can be limited by processes such as internal conversion, fluorescence and excited-state quenching.

The chain length of the polymerization can also be modified with reaction with oxygen or other adventitious impurities. There are other criteria to be considered which are not based on photochemistry but are nevertheless very important. These include toxicity, expense, and solubility.

1.7. PHOTOINITIATED CATIONIC POLYMERIZATION :

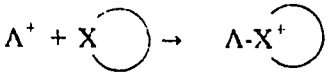
Modern cationic polymerization began about 40 years ago with the discoveries of cocatalysis but it was continued efforts of relatively few scientists in the fifties and early sixties who brought new life into investigations of cationic polymerization.

The predominance of transfer processes is one reason why cationic polymerizations have proved of limited value in the commercial synthesis of useful polymers. However, recent work has demonstrated the value of cationically initiated polymerization in the hardening of the surface coating.[32] In these cases the products are highly cross-linked resins which do not depend for their properties on the formation of high molecular weight linear polymers. Initiation of cationic polymerization involves the generation of a positively charged species with its attendant counterion having thermal stability and low nucleophilicity

$$AB \rightarrow A^+B^-$$

The charged electrophile can then either add to a susceptible monomer molecule producing a positively charged active centre or, less often, it can accept an electron, again yieding a propagation cation.

$$A^+ + CH_2=CHR \rightarrow ACH_2\text{-}C^+HR \qquad 24$$



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$$X = O,S,N$$

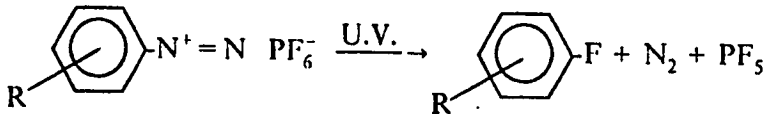
$$A^+ + CH_2=CHR \rightarrow A^{\cdot} + CH_2\text{-}C^{\cdot}HR \qquad 26$$

Recently, photoinitiated cationic polymerization using onium salts such as diazonium, diaryliodonium, and triarylsulphonium provide an efficient initiation of epoxide, lactones, cyclic ethers, silicones and acetals as well as adequate vinyl

monomers. Precisely how cationic polymerization is initiated is not known for any individual system but reaction of the cation radical intermediates with solvent or monomer is one likelihood.

(*1*). *Aryldiazonium salt photoinitiators* :

Aryl diazonium salts have long been known to be a class of photoactive chemicals. When aryl diazonium salts having anions such as PF_6^-, BF_4^-, AsF_6^-, PCl_6^-, SbF_6^-, are irradiated the resulting product is Lewis acid (eq. 27) which is capable of catalyzing the cationic polymerization reaction.



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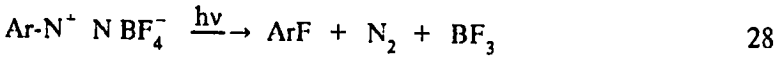
(1.1)

The following is one of the many mechanistic pathways which have been proposed to explain the Lewis acid catalyzed cationic polymerization of epoxide containing monomers.[11]



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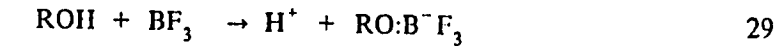

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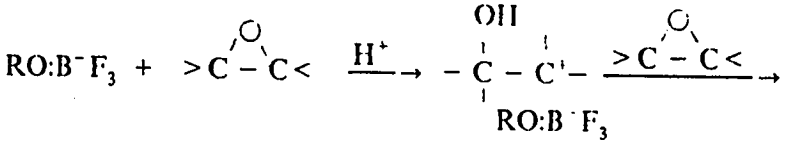

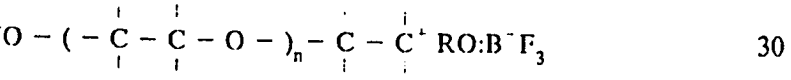

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The efficiency of aryldiazonium compounds as photoinitiators depends upon the structures of both the cationic and anionic portions of these salts.[12]

(2) *Diaryliodonium salts* :

Although the absorption spectra of Diaryliodonium salts in fig. (1.3) shows that the major bands occur at 200 and 240-250 nm, they are highly photosensitive compounds.

Diaryl iodonium salts having nucleophilic anions form non-acidic products after irradiation.[13] (eq.31). Photolysis in alcohol, however, was reported to form acid.[14] Crivello and Lam, at General Electric Company, found that the photolysis of diaryl iodonium salts having non-nucleophilic anions results in the formation of acidic species capable of polymerizing epoxy resins.[15(b)]

$$\text{Ph-I}^{+}\text{-Ph Cl}^{-} \xrightarrow{h\nu} \text{Ph-I} + \text{Ph-Cl (nonacidic)} \qquad 31$$

$$\text{Ph-I}^{+}\text{-Ph PF}_6^{-} \xrightarrow{h\nu} \text{Ph-I}^{+}\cdot\text{PF}_6^{-} + \text{Ph}\cdot \qquad 32$$

$$\text{Ph-I}^{+}\cdot\text{PF}_6^{-} + \text{RH} \rightarrow \text{Ph-I}^{+}\text{H PF}^{-}_{6} + \text{R}\cdot \qquad 33$$

$$\text{Ph-I}^{+}\text{H PF}_6^{-} \qquad \text{Ph-I} + \text{H}^{+}\text{PF}_6^{-} \qquad 34$$

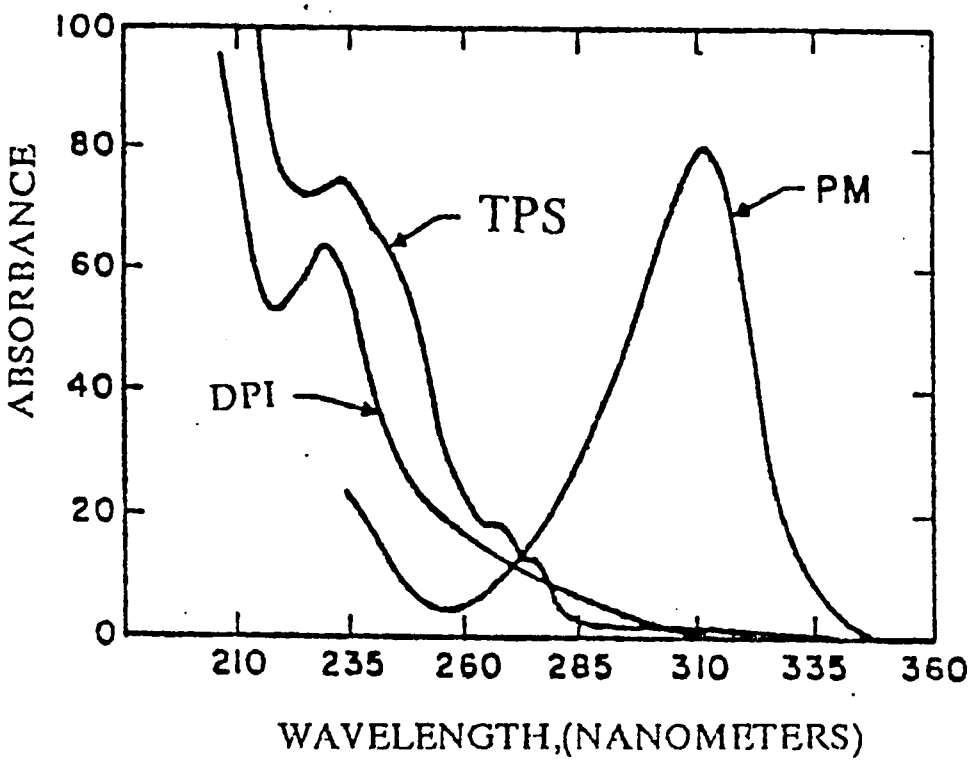


Figure (1.3) : UV absorbance spectra of onium salt photoinitiator (ref[2]). TPS = Triphenylsulphonium hexafluorophosphate, DPI = Diphenyliodonium hexafluorophosphate, PM = p-Methylbenzenediazonium hexafluorophosphate

(3). *Triarylsulphonium salts* :

Preparation and charaterization of triarylsulfonium salts have been reported[16] as early as 1891. These salts having general structure (1.2) are very stable and crystalline.

$$(Ar)_3 - S^+X^-$$

(1.2)

In the last few years workers at General Electric.[15f] 3M,[17] Imperial Chemical Industries Ltd[18] have reported the efficiency of triaryl sulphonium salts as photoinitiators in cationic polymerization.

Similar mechanism to the iodonium salts was proposed for the photolysis of triaryl sulphonium salts having non-nucleophilic anions.

$$ArI^{\cdot +}X^- + R\text{-}H \rightarrow ArI^+ - HX^- + R^{\cdot} \qquad 35$$

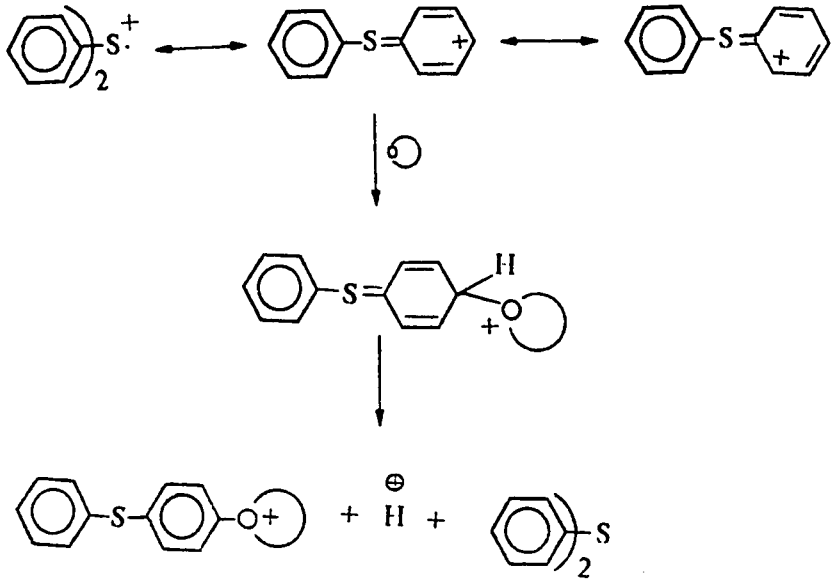
Aryl free radicals and cation radicals are the primary products of the photolysis of diaryl iodonium and triaryl sulphonium salts. The aryl iodonium and diaryl sulphonium cation-radicals are, therefore, the species ultimately responsible for initiating cationic polymerization. Crivello and Lam[19] have suggested that the arylsulphonium cation-radical interacts with the solvent or monomer, R-H, by hydrogen abstraction as shown in equation (36).

$$Ar_2S^{\cdot +}X^- + RH \rightarrow Ar_2S^+ - HX^- + R^{\cdot} \qquad 36$$

The species $Ar\text{-}I^+ - HX^-$ or $Ar_2S^+\text{-}HX^-$ can initiate polymerization directly or dissociate to give Bronsted acids.

Ledwith has proposed that aryl iodonium or diaryl sulphonium cation radicals

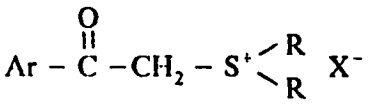
react with nucleophilic monomers as electrophiles[20] as shown in scheme (1.1)



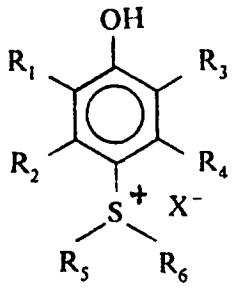
Scheme (1.1)

(4). *Dialkylphenacyl and dialkyl-4-hydroxyphenyl sulfonium salts* :

Dialkylphenacyl sulfonium salts[15(c)] (1.3) and dialkyl-4-hydroxy phenyl sulfonium salts[15(e)] (1.4) are two recent addition to the class of sulfonium salts which can be regarded as useful photoinitiators of cationic polymerization.

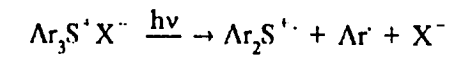


(1.3)



(1.4)

Investigation of the photolysis products and deuterium exchange studies[15(c),15(e)] have shown that the photochemistry of dialkylphenacylsulfonium and Dialkyl-4-hydroxyphenyl sulfonium salts is markedly different from that of the triarylsulphonium salts, while the latter compounds undergo reversible photoinduced carbon-sulphur bond cleavage (eq.37), the former compounds reversibly photodissociate to form the resonance stabilized ylids and protonic acids, HX (eq. 37,38) :



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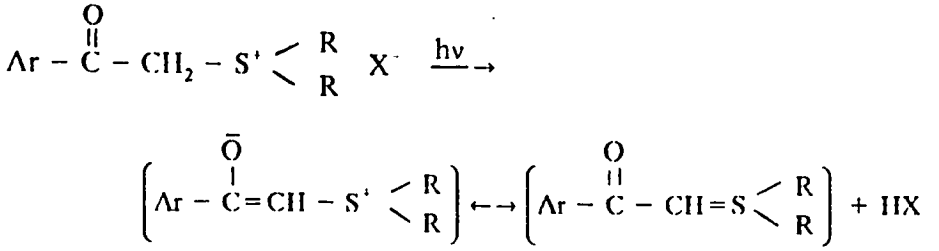

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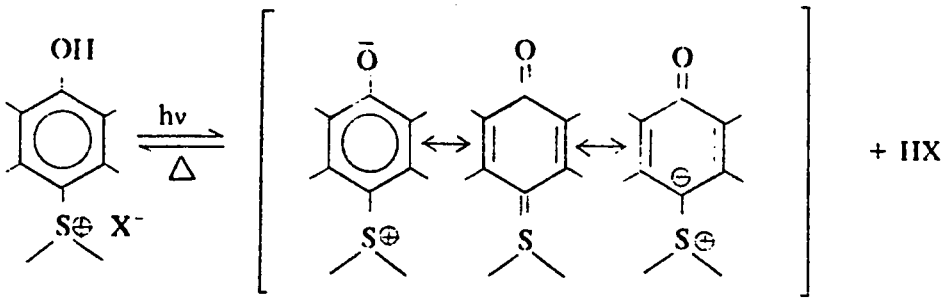
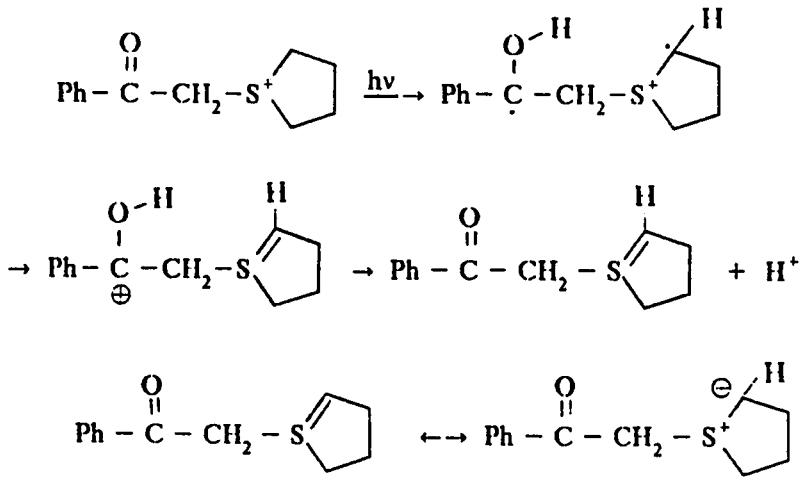


39

In both classes, the thermal back reaction competes with the forward photolysis and results in an overall steady-state concentration of ylid and acid. It is interesting to note that among related sulfonium salts, only those which can give similar resonance stabilized ylids are useful photoinitiators. The protonic acids, HX, formed during the photolysis of dialkyl phenacyl sulfonium and Dialkyl-4-hydroxy phenyl sulphonium salts are strongly solvated species. Further, the possibility that solvents may be involved in the formation of the acids by assisting in the removal of a proton from the excited sulfonium salts can not be ruled out.

Recent mechanistic studies with phenacyl sulfonium salts[21] have determined that the reactive excited state does not simply dissociate into ylid and Bronsted acid, as implied by equation (eq. 38). Rather, the mechanism in scheme (1.2) is proposed, which involve the (1) Intramolecular H-abstraction from γ-Carbon atom, (2) intramolecular electron transfer and (3) proton generation. The resulting ylid may, of course, be represented by two resonance contributors, as shown in scheme (1.2).



Scheme (1.2)

It has been noted that while dialkylphenacylsulfonium and dialkyl-4-hydroxy phenyl sulfonium salts photoinitiate the insitu polymerization of many monomers, photolysis of these sulphonium salts followed by the addition of the same monomers in the dark does not produce polymerization. In contrast, triaryl sulfonium salts by virtue of the irreversiblity of their photolysis initiate cationic polymerization regardless of whether the monomer is present during the photolysis or added subsequently.

(5). *Phosphonium salts* :

photolysis of triaryl phosphine[22,23] and tetra arylphosphonium salts[24] are some early photochemical studies of phosphorous compounds. Formation of products by the photolysis of triarylphosphine[22,23] was accounted for by assuming an initial homolysis of the carbon-phosphorous bond (eq.40).

$$Ar_3P \xrightarrow{h\nu} Ar^{\cdot} + Ar_2P^{\cdot} \qquad 40$$

$$Ar_2P^{\cdot} + C_6H_6 \rightarrow Ar_2PH + C_6H_5^{\cdot} \qquad 41$$

$$Ar^{\cdot} + C_6H_5^{\cdot} \rightarrow Ar\text{-}C_6H_5 \qquad 42$$

$$2Ar^{\cdot} \rightarrow Ar\text{-}Ar \qquad 43$$

$$2Ar_2P^{\cdot} \rightarrow Ar_2P\text{-}P\text{-}Ar_2 \qquad 44$$

The tetraarylphosphonium salts are themselves not stable towards radiation, thus when chloride salt was photolysed in benzene-ethanol mixture[24] biphenyl, diphenylphosphine and triphenylphosphine were obtained. These products have been explained by an electron transfer mechanism which produces phenyl radicals by an elimination from tetraphenyl phosphenyl (eq.45)

$$Ph_4P^+Cl^- \xrightarrow{h\nu} Ph_4P^{\cdot} + Cl^{\cdot} \rightarrow Ph_3P + Ph^{\cdot} + Cl^{\cdot} \qquad 45$$

The triphenyl derivatives of antimony, arsenic and bismuth have been reported to be effective initiators for crosslinking elastomeric polymers.[25] They were used as source of phenyl radicals when heated above 200 °C.

Mao et al[24] have reported the use of triphenyl phosphines in the photoinitiation polymerization of Methyl methacrylate and discussed various substituent effect[26] on

the polymerization rate. Only those monomers containing an α,β-unsaturated carbonyl group could be photoinitiated by triphenylphosphine and styrene was unaffected. The kinetic study of methyl methacrylate showed that the propagation was by free radical mechanism. The polymer contained one phosphorous atom per chain was shown by polymer analysis. Complex between the triphenylphosphine and each monomer was reported on the basis of U.V. spectra which acts as initiator for polymerization. The mechanism was proposed involving a light activated dipole interaction between the carbonyl oxygen and the phosphorous atom with the ultimate formation of methylmethacrylate type of free radical. Margan and coworkers[27] have reported that triphenylphosphine strongly accelerates the rate of thio/ene curing reaction and have also observed that addition of triphenyl phosphine to a system already containing benzophenone and benzoin ether as a photoinitiator resulted in a marked acceleration in cure. The proposed mechanism involved a charge-transfer complex as in equation (46,47)

$$RCH{=}CH_2 + :PPh_3 \xrightarrow{h\nu} RC^{\cdot}H - CH_2^{-}P^{+}{\cdot}Ph_3 \qquad 46$$

$$R'SH + RC^{\cdot}H - CH_2^{-}P^{+}{\cdot}Ph_3 \rightarrow R'S^{\cdot} + RCH_2 - CH_2^{-} + P^{+}{\cdot}Ph_3 \qquad 47$$

They also proposed that effect of phosphine mentioned above was due to the ability of such compounds to scavenge trace of sulfur and also dissolved oxygen from the system.

Few years back Tsuda et al,[28,29] studied the free radical polymerization of methyl methacrylate and styrene initiated by phosphonium salts having anion such as Br^-, Cl^- and BF_4^-. These polymerizations were terminated by the addition of benzoquinone as a radical scavenger. They reported that the photolysis of these

phosphonium salts gave the phenyl radical which initiated the free radical polymerization of styrene and MMA. On the other hand, tetraphenylphosphonium iodide did not initiate the photopolymerization of vinyl monomers. Further the initiation ability increased with the change of anions in the order $Br^- < Cl^- < BF_4^-$. This order coincides with the ease of photooxidation of anions.[30] Based on the effect of changing counter anion for initiation ability they proposed that a one electron transfer mechanism was reasonable in those initiation reactions. However, in the case of tetraphenylphosphonium tetrafluoroborate, they could not rule out the direct homolysis of P-Ph bond that gives the phenyl radical as the initiating species since BF_4^- is not an easily photooxidizable anion.[30] They also studied photoinitiating ability of binary system of ethoxycarbonylmethyltriphenylphosphonium chloride (TPPC) and triethyl amine and it was seen that TPPC has photoinitiation ability for MMA which is shown in scheme (1.3).

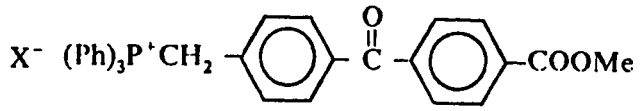
$$Cl^-P^+Ph_3-CH_2-COOEt \xrightarrow{Et_3N} Ph_3P^+-C^-H-COOEt \qquad 48$$

$$Ph_3P^+-C^-H-COOEt \xrightarrow{h\nu} Ph^\cdot + Ph_2P^{+\cdot}-C^-H-COOEt \qquad 49$$

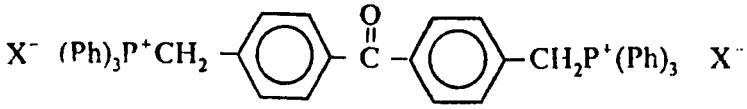
$$CH_2=CHX \xrightarrow{Ph^\cdot} -(-CH_2-CHX-)-_n \qquad 50$$

Scheme (1.3)

Photoinitiated polymerization of methyl methacrylate and styrene using p,p'-Bis ((triphenylphosphonio) methyl)benzophenone salt[31] (1.5, 1.6) which comprises chromophore and the para positional dissociable functionality was studied recently. This gives radical as well as cationic polymerization depending upon the irradiation wavelengths.



(1.5)



(1.6)

X = SbF_6, PF_6, Br, BF_4, AsF_6

It was observed that if the the reaction mixture was irradiated at 300 nm cationic polymerization of cyclohexeneoxide took place but if it was irradiated at 366 nm only free radical polymerization of methyl methacrylate took place. The effect of counterion, salt structure, and salt concentration were studied.

1.8. PHOTOSENSITIZATION OF ONIUM SALTS

Many condensed aromatic molecules and organic dyes are so called sensitizers for initiation of cationic polymerization with iodonium and sulphonium salts. Pappas and Jilek.[32] considered three possible mechanisms for photoinitiated cationic polymerization by photosensitization of onium salts.

(a) By classical energy transfer, which involves production of the exited state onium salts $(O)^*$, indirectly by energy transfer from the photoexcited photosensitizer (P^*)

$$P \rightarrow P^*$$

$$P^* + O \rightarrow P + O^*$$

energy required $E^*(P) > E^*(O)$

This may be discarded as a mechanism for photosensitization since the excitation energies of the photosensitizer used are lower than that of onium salt.

(b) Photosensitized homolytic bond cleavage of onium salts, which requires that the excitation energy of the sensitizer be greater than the homolytic bond dissociation energy of the salt.

$$P \rightarrow P^* \qquad 51$$

$$P^* + Ar_3S^+X^- \rightarrow [P.....Ar_3S^+X^-]^* \qquad 52$$

$$[P.....Ar_3S^+X^-]^* \rightarrow P^* + Ar_2S^{+\cdot}X^- + Ar^\cdot \qquad 53$$

$$Ar_2S^{+\cdot}X^- \rightarrow H^+X^- \rightarrow \text{polymer} \qquad 54$$

(c) Photosensitization by electron transfer is the most probable mechanism. This involves electron transfer from the excited state of the photosensitizer (P^*) to the onium salt.

$$P \xrightarrow{h\nu} P^{\bullet}$$

$$P^{\bullet} + Ar_3S^+X^- \rightarrow P^{+\cdot}X^- + Ar_3S^{\cdot} \quad 55$$

$$P^{+\cdot}X^- \xrightarrow{THF} H^+X^- + P + THF^{\cdot} \quad 56$$

$$H^+X^- \xrightarrow{THF} \text{polymer} \quad 57$$

$$Ar_3S^{\cdot} \rightarrow Ar_2S + Ar^{\cdot} \quad 58$$

For successful electron transfer process of excitation energy, $E^{\bullet}$, of the photosensitizer, P, must be greater than the sum of the energy required to oxidize (remove an electron) P, $E^{ox}(P)$ and the energy required to reduce (add an electron) the onium salt, O^+,$E^{red}(O^+)$.

i.e.

$$E^{\bullet}(P) > \sum E^{ox}(P) + E^{red}(O^+) \quad 59$$

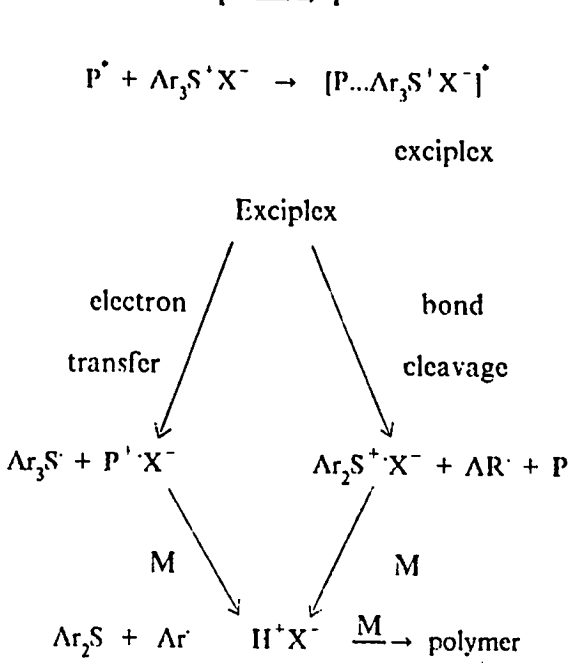
Therefore

$$E^{\bullet}(P)\text{-}E^{ox}(P) > E^{red}(O^+) \quad 60$$

The efficiency of electron transfer and initiator generation depends on other factors such as the lifetime of $P^{\bullet}$ and the reactivity of the resulting cation radical ($P^{+\cdot}$). Furthermore, the photosensitizer itself may interfere with the cationic polymerization as in the case of Michler ketone and acridone.[32]

There is also a possibility that photosensitized bond cleavage may accompany the electron transfer mechanism. Since photosensitized bond cleavage is expected to occur within an exciplex, in which its stability depends on charge transfer interactions, it appears that this mechanism can not be ruled out simply on the basis of the energetics of bond cleavage, i.e. the exciplex intermediate may undergo

electron transfer to the onium salt and/or bond cleavage of the onium salt to produce cation radicals which acts as precursors of an initiator species such as H^+X^-.



Scheme (1.4)

Recently Crivello[33] reported that dialkylphenacyl sulphonium and dialkyl-4-hydroxy sulphonium salt spectra can be broadened through the use of photosensitizers in the case of the dialkylphenacylsulphonium salts. Photosensitization by an electron transfer mechanism has been proposed. The key feature of this mechanism involves the electron transfer between the photosensitizer, P, and the salt to give a cation-radical species which then becomes the initiating species. The product of the reaction is a resonance stabilizes radical which eventually collapses by fragmentation (scheme 1.5).

$$P \xrightarrow{h\nu} P^{\bullet}$$

$$P^{\bullet} + ArCO\text{-}CH_2\text{-}S^{+}R_2X^{-} \rightarrow [P...ArCO\text{-}CH_2\text{-}S^{+}R_2X^{-}]^{\bullet}$$

$$[P...ArCO\text{-}CH_2\text{-}S^{+}R_2X^{-}]^{\bullet} \rightarrow ArCO\text{-}CH_2^{\bullet} + R_2S^{+}\cdot X^{-}$$

$$R_2S^{+}\cdot X^{-} \xrightarrow{M} \text{Polymer}$$

Scheme (1.5)

Condensed ring hydrocarbons, phenothiazines and those aromatic ketones having low oxidation potentials are active photoinitiators for those sulphonium salts. Confirmation of the mechanism shown was obtained by calculation of free energies for electron transfer from the electrochemical half-wave potentials and the triplet excitation energies by the relationship

$$\Delta G = [E^{ox}_{sens} - E^{red}_{onium}] - E^{*} \qquad 61$$

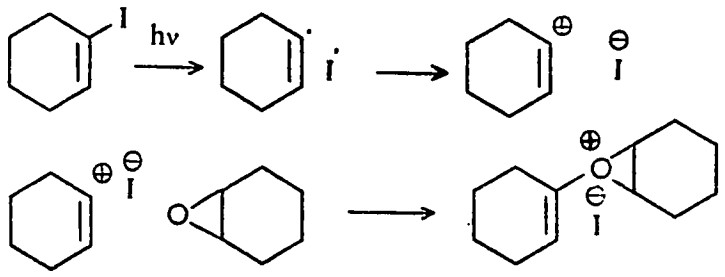
Where ΔG is the free energy of the electron transfer, E^{*} is the excitation energy of the photosensitizer, and E^{ox} and E^{red}_{onium} has been estimated to be of the order of 14.5 kcal/mol for dialkylphenacylsulphonium salt.[34] Another prove was obtained by the direct observation of the stable perylene cation radical when perylene was used as a photosensitizer for dialkylphenacylsulphonium salts. Perylene groups were also detected attached as end groups to polymers to polymers produced by these systems

The most modern method of promotion of cationic polymerization, employes photochemical radical sources, particularly those which have commercial applications in U.V. curable coatings,[35] such as benzoin alkyl ethers and alkoxy acetophenone in the presence of iodonium salts, where chain reactions lead to initiation of cationic polymerization.[36,37]

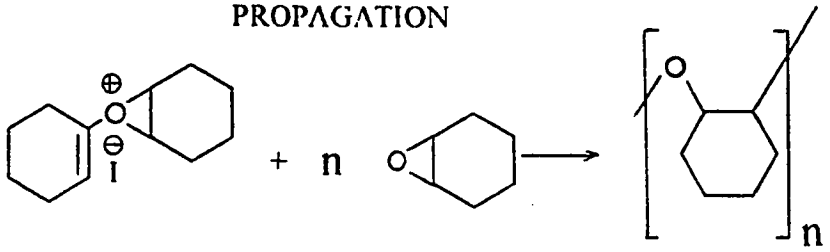
1.9. CATIONIC POLYMERIZATION OF CYCLOHEXENEOXIDE :

Photopolymerization of cyclohexene oxide in the presence of electron accepter was studied in a bulk system (in liquid as well as solid states). The polymerization was proved to proceed by cationic mechanism in both states by the effect of initiators.[38]

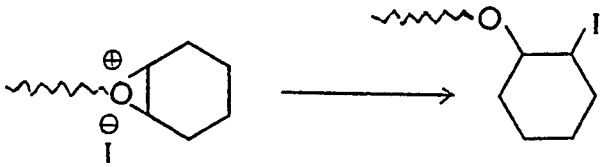
INITIATION



PROPAGATION



TERMINATION



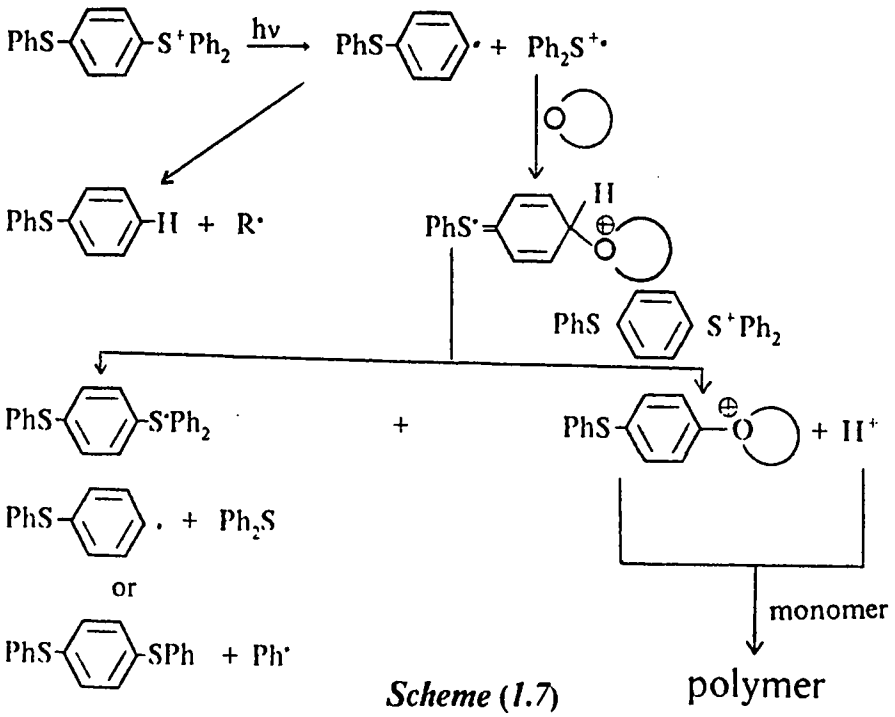
Scheme (1.6)

The polymerization in the presence of pyrometallic dianhydride or tetrahydrobenzene in methylene chloride proceeded by a cationic mechanism. Electron spin resonance (ESR) studies showed that the radical cation generated from the photoexcited electron donor accepter complex initiated the cationic

polymerization in this system.[39]

Kinstle and Tufts[40] have reported that irradiation of cyclohexeneoxide in the presence of 1-iodocyclohexene gives polycyclohexeneoxide and proposed the initiation mechanism shown in scheme (1.6). The highest conversion noted, as measured by the amount of polymer isolated by precipitation, was only 2-3%

Onium salts containing complex metal halide anions initiate polymerization of cyclohexeneoxide, for example, sulphonium salts and iodonium salts of AsF_6^- and PF_6^- were reported by Crivello.[15] Recently Ledwith et al[41,42] suggested mechanism for cationic polymerization of cyclohexeneoxide by triarylsulphonium as shown in scheme (1.7).



Scheme (1.7)

The absorption spectra of the polycyclohexeneoxide and salt photolysis products are shown in fig (1.6)

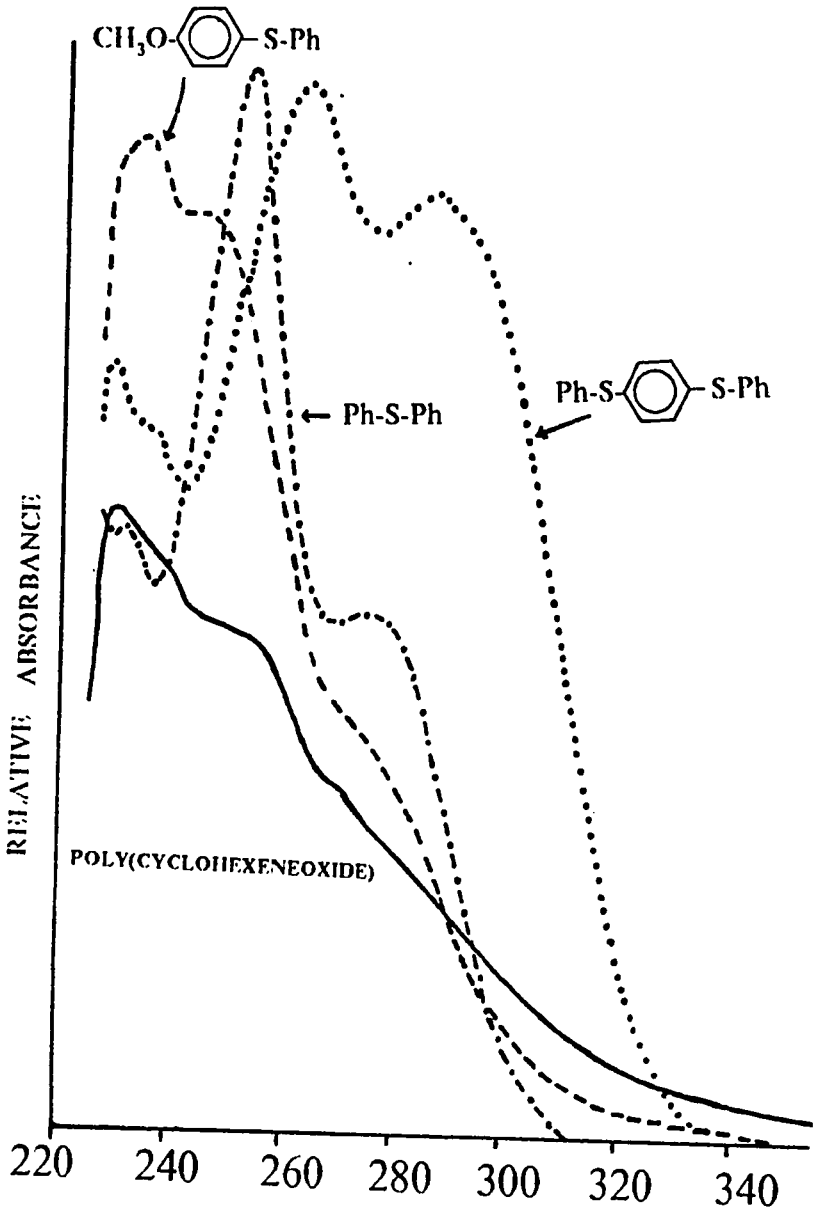


Figure 1.6 : Absorption spectra of dichloromethane (ref.[42]).

Photopolymerization of cyclohexeneoxide was also investigated with $Ph_3SiCOPh$-Aluminum complex-alcohol catalyst system.[43]

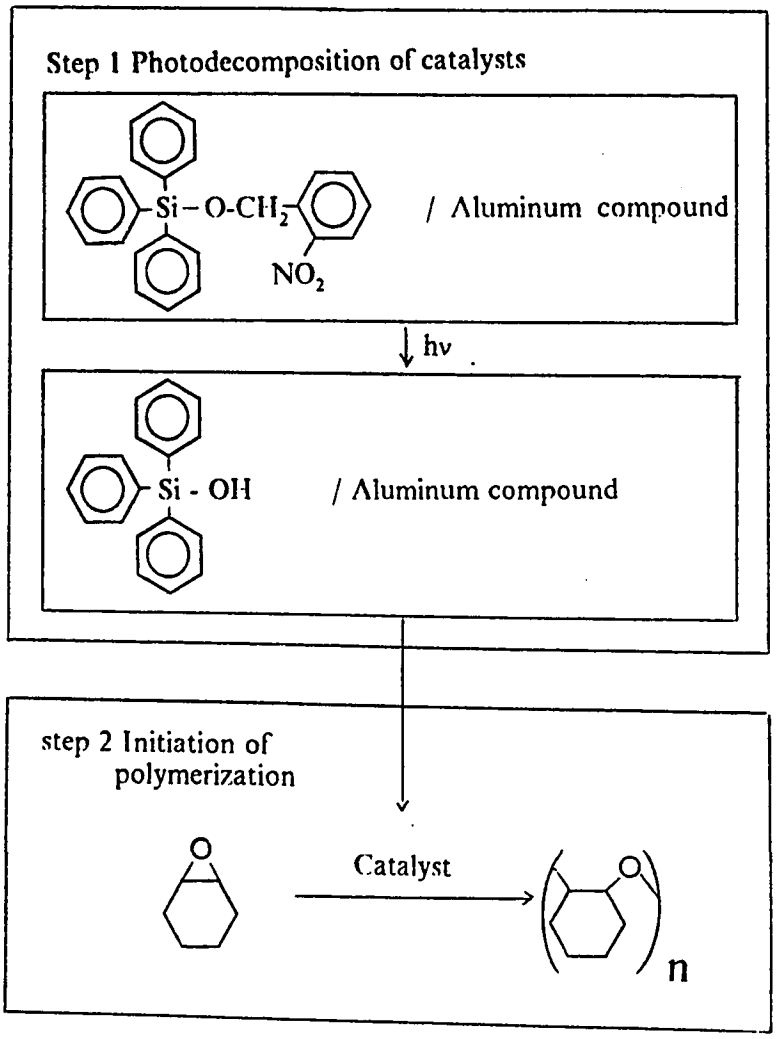
$$Ph_3SiCOPh \xrightarrow{h\nu + \text{alcohol}} Ph_3SiOH\text{-Al-complex}$$

$$\text{cyclohexene oxide} \xrightarrow[\text{Al-complex}]{Ph_3SiOH} \text{polymer}$$

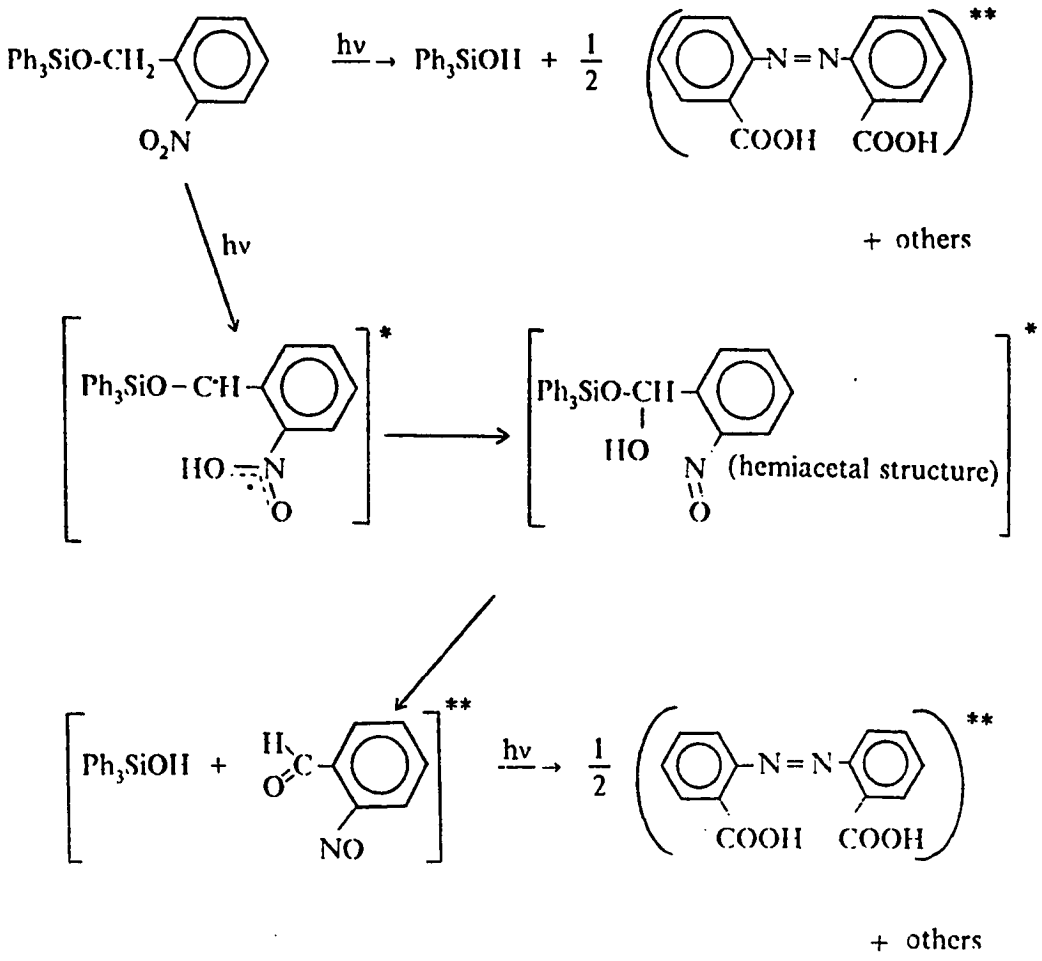
Scheme (1.8)

Alkyl aluminum, alkylaluminum modified by active hydrogen compounds, tantalum phenolate, AsF_6-complex, has been shown to act as catalyst in the photopolymerization of cyclohexeneoxide,[44] in the presence of $Ph_3SiCOPh$-Aluminum complex-alcohol catalyst system. The polymer conversion increased qualitatively with the increase in OH equivalent in the silanol compound.The polymerization behavior was changed by the choice of silanol compound and the catalytic activity was enhanced by the presence of a porous silica[45] which interacted with silanols. Hayase et al[46] reported another new photoinitiation catalysts consist of an aluminum compound and O-nitrobenzyltriphenylsilyl ether. The reaction mechanism is proposed as in scheme (1.9). The o-nitrobenzyltriphenylsilyl ether photodecomposes to form triphenylsilanol. The catalyst, which consist of an aluminum compound and the triphenylsilanol initiates the polymerization of epoxides. Epoxides do not polymerize at all in the absence of U.V. light. Photopolymerization was influenced by the structure of the aluminum compound, the wavelength of light used and the structure of the triarylsilyl ether. The relation between the silyl ether structure and the rate of photodecomposition of the silyl ether to triphenylsilanol (step 1) and the initiation of polymerization with the photodecomposed catalyst that consist of an

aluminum compound and triphenylsilanol (step 2) are reported.[47] The substitution of benzene ring affected the rate of step 2 more greatly than the rate of step 1. These substituents effects on the catalyst activity were explained in the terms of electronic and steric factors owing to position and variety of these substituents.

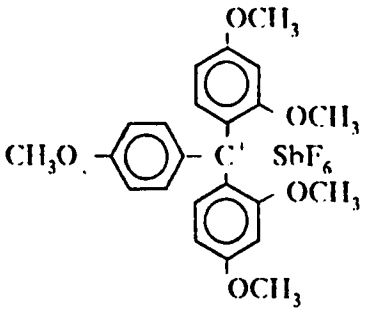


Scheme (1.9)

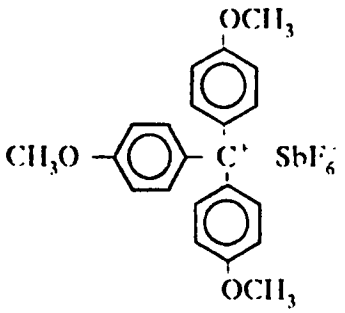


Scheme (1.10)

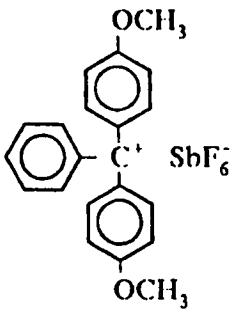
The photoinitiated cationic polymerization of cyclohexeneoxide in the presence of penta (1.8a), tri (1.8b) and dimethoxy trityl salts (1.8c) are reported and the effect of salt counterion, photolysis time, light intensity and variation of salt concentration on the polymerization rate are explained.[48]



1.8(a)



1.8(b)



1.8(c)

It was reported recently that new photoinitiator (1.5 and 1.6) initiates polymerization cationically when irradiated at 300 nm and free radical polymerization at 366 nm, the photodecomposition and photopolymerization characteristics and the mechanism were reported.[31] The characterization of a typical polycyclohexeneoxide obtained by the use of triphenylmethylhexafluoroarsinate ($Ph_3CAsF_6^-$)[49] and organozinc (e.g. $ZnEt_2$ or $[EtZnMe]_4$) compounds[50] were reported. It was found that polymerization was proceeded according to cationic mechanism.

1.10. POLYMERIZATION USING YLIDS

The term ylid may be defined as a class of compounds in which a carbanion is directly attached to a hetero atom bearing a positive charge. The hetero atom may be phosphorous, sulfur, arsenic or nitrogen. The phosphonium salts are more often converted to the ylids by treatment with a strong base such as butyl lithium,sodium amide, sodium hydride or a sodium alkoxide, though weaker bases may be used if the salt is acidic enough. The first phosphonium ylid to be studied was that obtained by Michaelis in 1899 on treatment of phenacyltriphenyl phosphonium bromide with sodium hydroxide solution[51] (eq.62).

$$Ph\text{-}CO\text{-}CH_2\text{-}Br + Ph_3P \rightarrow Ph\text{-}CO\text{-}CH_2\text{-}P^+Ph_3Br^-$$

$$\xrightarrow{NaOH(aq)} Ph\text{-}CO^- = CH\text{-}P^+Ph_3 \qquad 62$$

(1.9)

A number of structures were suggested for this stable ylid until in 1957, Ramirez and Dershowitz proposed the now accepted resonance hybrid of the following forms[52] (scheme 1.11a,b,c).

$$Ph\text{-}CO\text{-}CH=PPh_3 \longleftrightarrow Ph\text{-}CO\text{-}CH^- - P^+Ph_3 \longleftrightarrow Ph\text{-}CO^- = CH\text{-}P^+Ph_3$$

(a) (b) (c)

Scheme (1.11)

If electron withdrawing centres are conjugated with the ylidic carbon atom, further dipolar structure such as (b) and (c) may make major contributions to the overall structure. Delocalization of the negative charge in this way frequently leads to the ylid beeing isolable. Such ylids are commonly described as stable ylids. Many ylids are not, however, isolable because of their high reactivity, in particular their very ready hydrolysis.

Whereas much information has been published about phosphonium ylids, relatively little attention has been paid to arsonium ylids. Arsonium ylids such as (1.10) are relatively easy to prepare, and are more reactive than analogous phosphonium or sulphonium ylids in the Wittig reaction, in which they may provide alkenes or epoxides depending on the nature of substituent on both the ylidic carbon atom and the arsenic atom, and also to some extent on the solvent used.

$$CH_3\text{-}CO\text{-}CH=AsPh_3 \longleftrightarrow CH_3\text{-}CO^- = CH\text{-}As^+Ph_3$$

(1.10a) (1.10b)

Infra-red and NMR spectra for a series of diphenyl sulphonium, triphenyl phosphonium and triphenyl arsonium derivatives suggests that arsonium ylids are more dipolar than their phosphonium and sulphonium analogues.[53,54]

Nagao et al[55] reported that P-phenyl bond is broken first in the photolysis of the ylid (1.11), and that bond fission depends on the wavelength of the exciting light.[56]

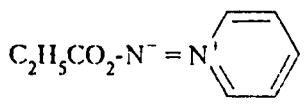
CH_3-CO-CH=PPh_3

(1.11)

Recently there has been growing interest in the field of polymer-ylid chemistry. Kondo and coworkers reported that triphenyl phosphonium ylid,[57] (1.12), diphenyl sulphonium ylid,[58] DPSY (1.13), diphenyl oxosulphonium bis(methoxycarbonyl)methylide ylid,[59] POSY (1.14) and t-ethoxycarbonyliminopyridinium ylid[60] IPYY (1.15) worked as initiator for the polymerization of methyl methacrylate and styrene.

$C_2H_5CO_2CH^-P^+Ph_3$ $(CH_3CO_2)C^-S^+Ph_2$ $(CH_3CO_2)C^-SO^+Ph_2$

(1.12) (1.13) DPSY (1.14) POSY



(1.15) IPYY

These ylids are used as a source of phenyl radicals when irradiated by a high pressure mercury lamp. Radical polymerization mechanism was confirmed from the effect of the radical scavenger and the kinetic study of the MMA and styrene

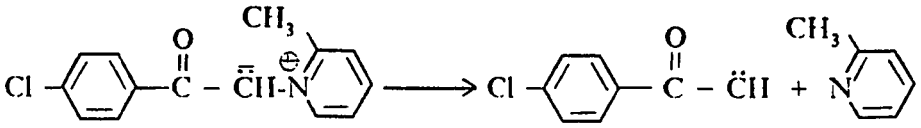
copolymerization and product of ylid analysis.

The kinetics of thermal polymerization of α− methyl styrene initiated by para amino benzyltriphenyl phosphonium ylid (1.16) has been studied,[61] and various kinetic parameters such as rate of reaction, rate constant have been determined.

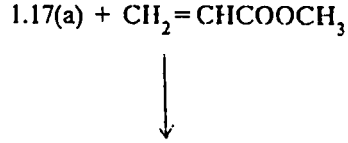
$$H_2N\text{-}C_6H_4\text{-}CH=PPh_3$$

(1.16)

Later work by Srivastava et al[62] showed that thermal polymerization of methyl acrylate by heterocyclic ylid (1.17) follows a nonideal kinetics of radical ploymerization due to additional primary radical termination which is shown in scheme (1.12).



1.17(a)



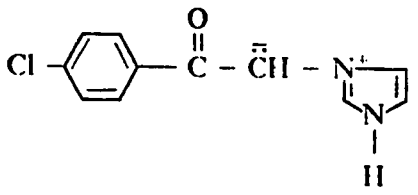
p- Cl $C_6H_4CO\text{-}CH^{\cdot} - CH_2 - CH^{\cdot}COOCH_3$

diradical

$p - Cl - C_6H_4CO - CH=CH - CHCOOCH_3 + H^+$

Scheme (1.12)

They extend this work by using imidazolium ylid[63] imidazolium-p-chlorophenacylide (ICPY) (1.18)



(1.18)

as thermal initiator for methacrylate (MA) ploymerization in dioxane at 60 °C with a view to obtain higher conversion without generation and autoacceleration. Termination was initiator dependant and transfer of the degradative type reasonably explained the kinetic non-ideality.

1.11. PHOTOINITIATED RADICAL POLYMRRIZATION :

A typical photochemically induced free radical polymerization is outlined

Photolysis

$$R\text{-}R \xrightarrow{h\nu} 2R^{\cdot} \qquad 63$$

initiation

$$R^{\cdot} + CH_2{=}CHR \rightarrow R\text{-}CH_2\text{-}CHR^{\cdot} \qquad 64$$

propagation

$$R\text{-}CH_2CHR^{\cdot} + nCH_2{=}CHR \rightarrow R\text{-}(\text{-}CH_2\text{-}CHR\text{-})_n\text{-}CH_2\text{-}CHR^{\cdot} \qquad 65$$

Termination

$$2R\text{-}(\text{-}CH_2\text{-}CHR\text{-})_n\text{-}CH_2\text{-}CHR^{\cdot} \rightarrow [R\text{-}(\text{-}CH_2\text{-}CHR\text{-})_n\text{-}CH_2\text{-}CHR\text{-}]_2 - \qquad 66$$

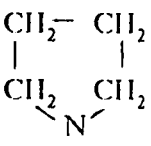
The key step in this process is the absorption of light by the photoinitiator compound, R-R, to generate two radical fragments. once radicals are produced by photolysis, they participate in the usual free radical vinyl polymerization processes

of initiation, propagation, and termination. It is important to note that this process is energy efficient.

1.11.1. Monomers :

In free radical polymerization most useful monomers which contain double bonds have them in the form of a 1,2-ene group, i.e. $CH_2=CXY$, where XY are substituents. During the polymerization the π bond part of the double bond is destroyed and polymerization occurs by the formation of two new σ bonds. Free radical polymerization is possible if the substituents X and Y help to stabilize a propagating free radical. Such substituents are either electron withdrawing (e.g. Cl, COOR) or conjugating (e.g. Ar). The vinyl groups of most value in free radical polymerization are shown in table (1.1).

Table (1.1) : Examples of vinyl monomers CH_2CXY

X	Y	Name
H	COOR	Acrylate ester
CH_3	COOR	Methacrylate ester
H	C_6H_5	Styrene
H	$OCOCH_3$	Vinyl acetate
H		N-Vinyl pyrrolidone

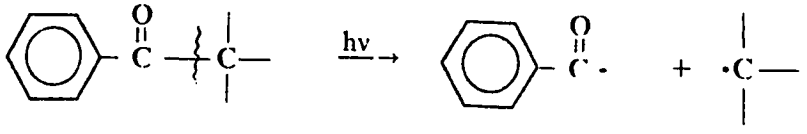
1.11.2 Photoinitiators :

A large number of compounds have been suggested for use as photoinitiators.[64] Relatively few have been commercially successful, largely because of the difficulty of meeting the criteria which have been listed in section (1.5).

Almost all of those which have achieved lasting success have been aromatic carbonyl compounds.[65] These have absorption spectra which allow them to respond well to the wavelengths emitted by the medium pressure mercury lamp, and their excited states are often very reactive. Photoinitiators may be divided into two main groups depending on whether the process by which radicals are produced is unimolecular or bimolecular. Unimolecular radical production implies a fragmentation process. Bond broken may be C-C, C-X, C-S, S-S, C-O, N-O, S-X (X = halogen).

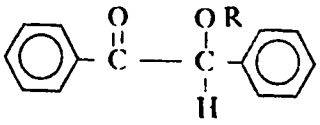
(i) Unimolecular radical production :

Examples of aromatic carbonyl compounds which produce radicals by unimolecular processes and have become commercially successful, are shown in figure (1.7). Most but not all fragment by α or Norish type-I cleavage (eq.67) :

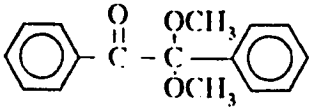


67

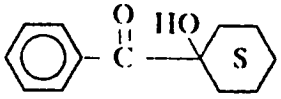
for example benzoin ethers (1.19) have been the most extensively studied and used initiators in the ultraviolet curing of lacquers for application to paper (for record sleeves and book covers).



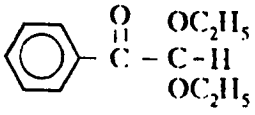
alkyl benzoin ether
trigonal 14 R = butyl



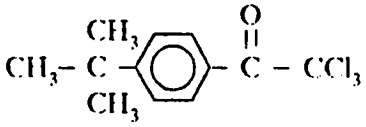
α, α-dimethyl α -phenyl
acetophenone
Irgacure 651



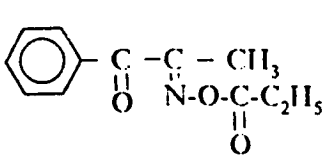
1-benzoylcyclohexanol
Irgacure 184



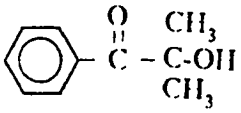
α, α-diethoxyacetophnone



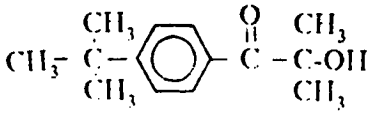
α,α,α-trichloro-4-t-butyl
acetophenone
trigonal PI



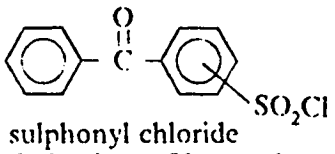
1-phenyl-1,2-propanedione-
2-O-ethoxycarbonylester
Quantacure PDO



α,α-simethyl-α-hydroxy
acetophenone
Darocur 1173

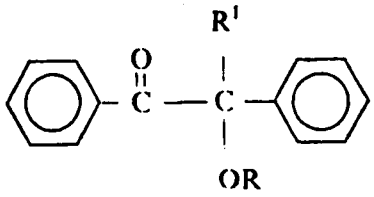


α,α-simethyl-α-hydroxy
4-t-butyl-acetophenone
Darocur 1116



sulphonyl chloride
derivatives of benzophenone

Figure 1.7 Aromatic carbonyl compounds which act as photoinitiators by a unimolecular process. Darocur is a trademark of E. Merck; Irgacure is a trademark of Ciba Geigy; Trigonal is a trademark of Ward Blenkinsop.



(1.19)

Benzoin itself (R = R_2 = H) is a rather poor photoinitiator and has a low solubility in resin-monomer systems. It was found that when R_1 = H, the order of merit for varying R_2 was alkyl > aryl > H > COR. Alkyl ethers are therefore most effective and alkyl esters least effective. The effectiveness of bezylic substituents can be related quantitatively to the Hammet σ factor.[66]

(ii) Bimolecular radical production :

Other types of carbonyl compound in figure (1.8) have also found wide application as photoinitiators, for example, benzophenone, thioxanthone, and 2-chlorothioxanthone produce initiator radical through hydrogen abstraction from a suitable donor.

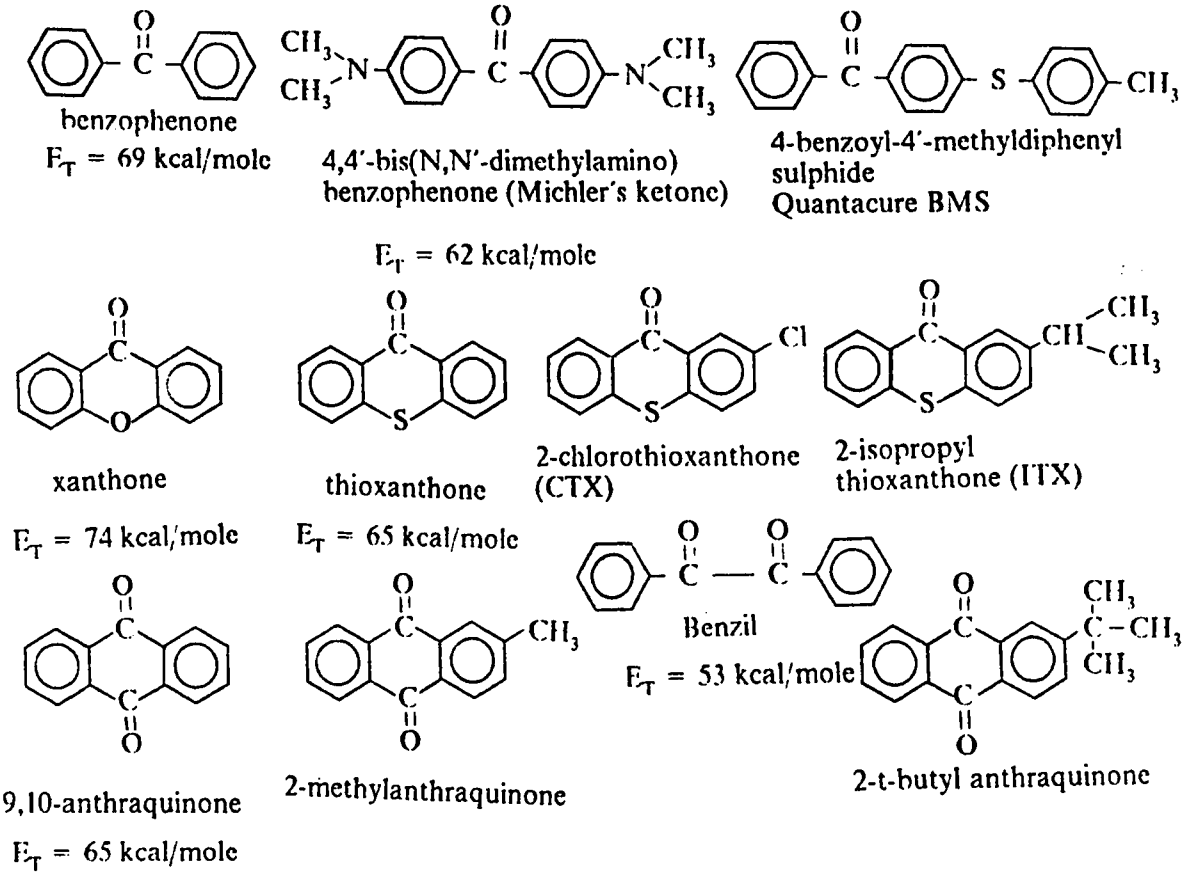


Figure 1.8 Aromatic carbonyl compounds which act as photoinitiators by a bimolecular process.

The reactions that occur between the photoinitiator (P) and hydrogen donor (RH) are as follows :

$$P \xrightarrow{h\nu} {}^1P^* \qquad 68$$

absorption

$${}^1P^* \rightarrow {}^3P^* \qquad 69$$

Intersystem crossing

$${}^1P^* \rightarrow P \qquad 70$$

singlet Decay

$${}^3P^* + RH \xrightarrow{Q} PH^{\cdot} + R^{\cdot} \qquad 71$$

hydrogen abstraction

$${}^3P^* \rightarrow P \qquad 72$$

quenching

Hydrogen abstraction is envisaged as occuring from the triplet state, because its radical character is more developed than that of excited singlet state, and it also has a longer life time during which reaction can take place. The efficiency of the reaction depends on (i) the intersystem crossing efficiency, (ii) the type of triplet formed, (n,π^*) or (π,π^*), and (iii) the polarity of the solvent.

Particularly hydrogen-atom donors are those in which (i) the active hydrogen atom is directly attached to sulphur, as in thiols (RSH), or (ii) a hydrogen atom is in a position alpha to an oxygen atom, as in alcohols (R_2CHOH) or ethers (R_2CHOR'), or alpha to a nitrogen atom, as in tertiary amines ($R_2CHNR'_2$). In the case of alcohols and ethers, hydrogen abstraction occurs by reaction with (n,π^*) triplets, which have more strongly developed radical character than the (π,π^*) states. It is important in practice to recognize that quenching of the

triplet state by atmospheric oxygen can be more efficient than the initiating process (hydrogen abstraction). Michler's Ketone (MK) and its derivatives possess both diaryl ketone and tertiary amino groups, and so combine both features in one molecule. It is therefore possible in principle, for one molecule of MK to abstract hydrogen from another molecule MK to form two radicals, however, MK on its own is a poor photoinitiator[67] because it functions poorly as a ketone because of the electron rich amino groups and it is found that MK works best as a synergistic mixture with benzophenone. Intersystem crossing to the triplet state takes place with unit efficiency.[68]

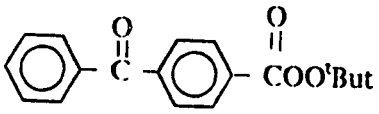
$$BP + MK^{*} \rightarrow [BP^{\delta-}....MK^{\delta+}]^{*} \quad \begin{matrix} \nearrow \text{ketyl radical from BP} \\ \searrow \text{amine radical from MK} \end{matrix} \qquad 73$$

MK has an absorption spectrum which is markedly dependant on the polarity of the solvent. It has a very strong absorption at 365 nm in ethanol and 335 nm in benzene. The mixture of benzophenone and Michler's ketone has found to be effective in pigmented ink when the two components are intimately mixed before incorporation in ink vehicle.

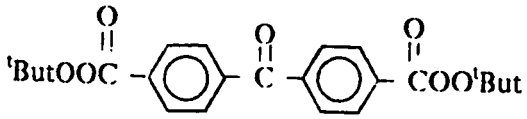
Thioxanthone derivatives are also effective initiators in formulations containing organic pigments. The presence of the sulphur atom allows a broad moderately large absorption between 360 nm and 400 nm with peak at 385 nm.

(iii) Miscellaneous systems :

Benzophenone mono (1.20) and dipersesters[69] (1.21) and aromatic perester[70] (1.22-1.25) were reported recently to undergo exclusive cleavage of the O-O bond and are used as a photoinitiator for styrene and methylmethacrylate polymerization.[70]

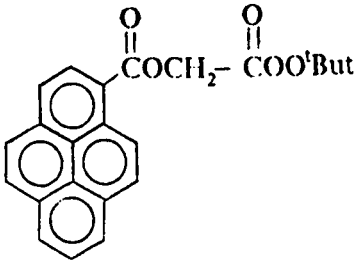


(1.20)



(1.21)

R = CH_3, CH_3O, H, $BrCH_2$



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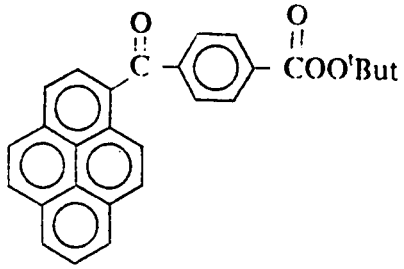

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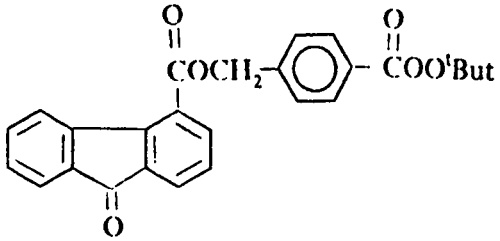

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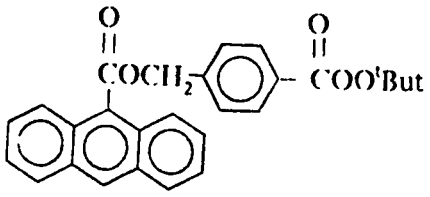
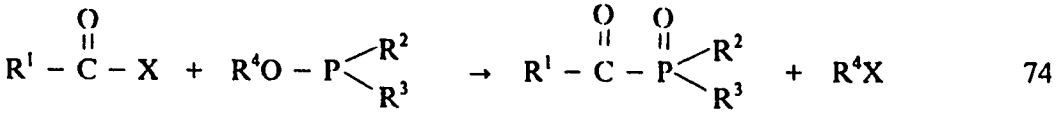


(1.23)

Acylophosphine oxide derivative have been reported as useful photoinitiators for the polymerization of acrylate and unsaturated polyesters-styrene composition.[71]



74

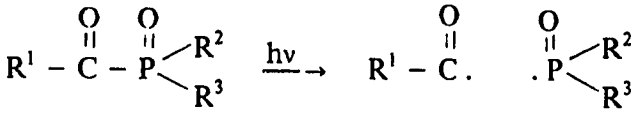
R^1 = alkyl, aryl, heterocyclic

R^2 = alkyl, cycloalkyl, aryl, heterocyclic

$R^2 = R^3$ = alkoxy, aryloxy, aralkoxy

R^4 = alkyl, cycloalkyl

X = Cl, Br



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1.12. OBJECTIVES

Very recently there has been a significant growth of interest in the use of onium salts such as triarylsulphonium ($Ar_3S^+MX_n^-$), diaryliodonium salts ($Ar_2I^+MX_n^-$) and aryldiazonium salts ($ArN_2^+MX_n^-$) as photoinitiators for cationic polymerization of epoxide monomers.

The main objective of the work described in this thesis was the synthesis, characterization and use of triaryl phosphonium and arsonium salts containing a specific chromophore unit such as aromatic carbonyl (e.g. phenacyl) or aromatic hydrocarbons (e.g. Anthracene) as photoinitiators for the cationic polymerization of epoxide (e.g. cycloheneoxide) and vinyl monomers such as styrene and p-methyl styrene. The interaction of these initiators with radically susceptible monomers such as methyl methacrylate was examined and to examine further the thermal stability of these salts in presence of the above monomers.

A parallel study was also carried out on the photosensitization of these salts and on the interaction of the ylid of these salts with the examined monomers. Particular attention to be directed at the influence of counterions and salt structure in determining the apparent activity of these new class of photoinitiators on the rate of polymerization.

CHAPTER 2

EXPERIMENTAL

2.1 Purification of materials

(1) Solvents

(i) Dichloromethane :

Commercially available (Fluka A.G.) dichloromethane was washed twice with concentrated H_2SO_4 then with water, twice with 5% (w/v) NaOH and finally with deionized water. The washed material was left overnight over sodium hydroxide pellets and calcium chloride granules. NaOH pellets and calcium chloride granules were removed by ordinary filtration. Again $CaCl_2$ was added and refluxed using fractionating column and condenser attached with drying tube. Finally methylene chloride distilled over calcium hydride (b.p. 39.5- 40.5 °C) was stored in coloured container in dark.

(ii) Benzene :

Commercial grade (Fluka A.G.) benzene was shaken successively with

concentrated sulphuric acid, until there was no change in colour of the acid, thus indicating that the thiophene had been removed. The benzene was then shaken with deionized water, dilute sodium hydroxide and again with deionized water. The washed benzene was left standing overnight over molecular sieve, then fractionally distilled from calcium hydride. The middle fraction (b. p. 80.0°C) was collected and stored over clean sodium wire.

(iii) Methyl alcohol :

Commercially available grade (Fluka A.G.) was used in polymer precipitation as received.

(iv) Diethyl ether :

Anhydrous grade (Fluka A.G.) was used as received

(v) Hexane :

Commercially available HPLC grade (Fluka A.G.) was used as received.

(2) *Monomers*

(i) Styrene :-

The inhibitor was removed from styrene (Fluka A.G.) by washing it five times with a 20% (w/v) solution of NaOH. The monomer was thoroughly washed with deionized water and dried over anhydrous calcium chloride. The styrene was then further dried with calcium hydride and distilled under reduced pressure with a nitrogen bleed immediately before use.

(ii) Methylmethacrylate :-

Methylmethacrylate (Fluka A G) freed from inhibitor by washing it five times with 10% (w/v) aqueous NaOH to remove hydroquinone inhibitor, followed by repeated washing with deionized water to constant pH. The monomer was dried overnight over anhydrous calcium chloride and was kept in round bottomed flask over calcium hydride in a stoppered flask. The methylmethacrylate was distilled under reduced pressure with a nitrogen bleed just prior to use.

(iii) P-Methyl styrene:-

P-Methyl styrene (Fluka A G) was dried over CaH_2 and was distilled twice under reduced pressure and was stored in coloured container in the refrigerator.

(iv) Cyclohexene oxide :-

Cyclohexene oxide (Fluka A G) was dried over calcium hydride and fractionaly distilled before use. The middle fraction of distillation (b.p. 130°C) was collected in a coloured container. The pure material was stored in refrigerator.

2.2 Starting materials

Triphenyl phosphine, triphenyl arsine, p-bromophenacyl bromide, benzyl chloride, p-nitrobenzyl bromide, 9-chloromethyl anthracene, 2-bromomethyl anthraquinone, potassium hexafluorophosphate, potassium hexafluoroantimonate and triethyl amine were obtained from Fluka A G. Chloromethyl styrene (Poly Sciences Inc.), phenacyl bromide, and p-phenylphenacyl bromide were obtained from Eastman; pyrene, from Chem Services; N-methyl phenothiazine from Pfaltz &

Bauer Inc. and pyridine from BDH Chemicals Ltd.

2.3 Initiators synthesis

(I) Phosphonium salts

All the phosphonium salts reported in table (3.1) were synthesized by refluxing equimolar amount of their respective bromides or chlorides, mentioned in the starting materials, and triphenylphosphine for 4 h in benzene or 12 h in chloroform in the case of chloride. The reaction mixture was stirred at room temperature and was recovered by precipitation in diethyl ether. For other salts such as phenacyltriphenyl phosphonium bromide, the mixture was refluxed in benzene and the salt was recovered by keeping the refluxed material overnight at room temperature. Further purification was done either by precipitation of chloroform solution of salt in diethyl ether or hexane or recrystallization from benzene itself.

The bromide or chloride anions of phosphonium salts formed were replaced by the corresponding PF_6^- and SbF_6^- counterions by reaction of the bromide or chloride salts with equimolar amount of KPF_6 or $KSbF_6$. The chloride or bromide salts were stirred with KPF_6 or $KSbF_6$ in water/methanol mixture (1:1 v/v). Excess of the potassium salt was used to ensure complete formation of the required counter ion. After stirring for 3 h at room temperature the salt was filtered off, washed with water several times, dissolved in dichloromethane and dried over calcium chloride. The solvent was removed by rotavap and the salt was dried under vacuum at room temperature. Further purification was achieved by dissolving the salts in small volume of dichloromethane and reprecipitating them with excess of hexane. Uncorrected melting points taken on Buchi 510 m.p. apparatus and percentage

yields for the formation of salts are reported later.

(i) Phenacyltriphenylphosphonium bromide (1):-

5.97 g of phenacylbromide (3.00×10^{-2} mole), 8.0 g of triphenylphosphine (3.05×10^{-2} mole) were dissolved in 100 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (92%). Melting point 274-276 °C (lit.[72] 269-271 °C). IR spectrum revealed the CO stretch 1660 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.5 (2H, d, J= 12.47 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 254 nm (8.80×10^5), 325 nm (3.32×10^5), 234 nm (3.50×10^5), 232 nm (8.00×10^5) and 231 nm (3.90×10^5).

(ii) Phenacyltriphenylphosphonium hexafluoroantimonate (2) :-

2.3 g of phenacyltriphenylphosphonium bromide (5.00×10^{-3} Mole), 1.5 g of $KSbF_6$ (5.45×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (82%). Melting point 144-146 °C. IR spectrum revealed the CO stretch 1687 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.6 (2H, d, J= 13.79 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 257 nm (2.33×10^4), 234 nm (4.4×10^4), 232 nm and (6.50×10^4).

(iii) Phenacyltriphenylphosphonium hexafluorophosphate (3) :-

2.3 g of phenacyltriphenylphosphonium bromide (5.00×10^{-3} Mole), 1.0 g of KPF_6 (5.43×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (91%). Melting point 170-171 °C. IR spectrum revealed the CO stretch 1682 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.3 (2H, d, J= 13.3 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 257 nm (2.56×10^4), 236 nm (2.98×10^4) and 230 nm (3.7×10^4).

(iv) p-Bromophenacyltriphenylphosphonium bromide (4) :-

5.56 g of p-bromophenacylbromide (2.00×10^{-2} mole), 5.5 g of triphenylphosphine (2.10×10^{-2} mole) were dissolved in 75 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (91%). Melting point 222-224 °C (lit.[73] 192 °C). IR spectrum revealed the CO stretch 1673 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.4 (2H, d, J= 13.3 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 269 nm (0.62×10^4) and 229 nm (4.00×10^4).

(v) p-Bromophenacyltriphenylphosphonium hexafluoroantimonate (5) :-

2.7 g of p-Bromophenacyltriphenylphosphonium bromide (5.00×10^{-3} Mole), 1.5

g of $KSbF_6$ (5.45×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (83%). Melting point 166.5168 °C. IR spectrum revealed the CO stretch 1678 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.3 (2H, d, J= 12.3 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm (4.11×10^4), 257 nm (2.23×10^4) and 229 nm (4.63×10^4).

(vi) p-Bromophenacyltriphenylphosphonium hexafluorophosphate (6) :-

2.7 g of p-Bromophenacyltriphenylphosphonium bromide (5.00×10^{-3} Mole), 1.0 g of KPF_6 (5.43×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (81%). Melting point 209-209.5 °C. IR spectrum revealed the CO stretch 1673 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.2 (2H, d, J= 13.8 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm ($3.85 \times 10^{4)}$, 269 nm (3.78×10^4), 229 nm and (4.07×10^4).

(vii) p-Phenylphenacyltriphenylphosphonium bromide (7) :-

2.75 g of p-phenylphenacylbromide (1.00×10^{-2} mole), 2.8 g of triphenylphosphine (1.07×10^{-2} mole) were dissolved in 75 ml of benzene in 40 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (58%). Melting point 125-125.5 °C. IR spectrum revealed

the CO stretch 1681 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.4 (2H, d, J= 12.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 309 nm ($2.64x10^5$), 305 nm ($2.71x10^5$), and 235 nm ($3.23x10^5$).

(viii) Acetonyltriphenylphosphonium chloride (8) :-

Commercially available form Fluka A G. Melting point was 243.7 °C and was used as it is and UV absorption maxima λ_{max} and extinction coefficients ε_{max} are at 273 nm ($5.60x10^4$), 267 nm ($6.75x10^4$), 258 nm ($6.75x10^4$) and 229 nm ($3.19x10^5$) respectively in dichloromethane.

(ix) Acetonyltriphenylphosphonium hexafluoroantimonate (9) :-

1.77 g of Acetonyltriphenylphosphonium chloride (5.00×10^{-3} Mole), 1.5 g of $KSbF_6$ (5.45×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (97%). Melting point 154-155 °C. IR spectrum revealed the CO stretch 1700 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.7 (2H, d, J= 12.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm ($8.70x10^4$), 268 nm ($8.80x10^4$) and 235 nm ($8.40x10^4$).

(x) Acetonyltriphenylphosphonium hexafluorophosphate (10) :-

1.77 g of Acetonyltriphenylphosphonium chloride (5.00×10^{-3} Mole), 1.0 g of KPF_6 (5.43×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used

was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (98%). Melting point 160-161 °C. IR spectrum revealed the CO stretch 1717 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.8 (2H, d, J= 12.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm ($2.81x10^4$), 268 nm ($3.40x10^4$), 251 nm ($1.08x10^4$), and 235 nm ($9.10x10^4$).

(xi) 9-Methyleneanthracenyltriphenylphosphonium chloride (11) :-

1.13 g of 9-chloromethylanthracene (5.00×10^{-3} mole), 1.5 g of triphenylphosphine (5.73×10^{-3} mole) were dissolved in 25 ml of benzene in 100 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (61%). Melting point 285-286 °C. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.5 (2H, d, J= 13.5 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 400 nm ($7.35x10^4$), 380 nm ($7.42x10^4$), 375 nm ($7.35x10^4$), 360 nm ($6.08x10^4$), 315 nm ($3.49x10^4$), 260 nm ($7.20x10^4$), 255 nm ($7.14x10^4$) and 235 nm ($6.21x10^4$).

(xii) 9-Methyleneanthracenyltriphenylphosphonium hexafluoroantimonate (12) :-

1.22 g of 9-Methyleneanthracenyltriphenylphosphonium chloride (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume.

The salt was recovered as mentioned in the general procedure (95%). Melting point 246-247 °C. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.8 (2H, d, J= 14.3 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 400 nm ($7.82x10^4$), 380 nm ($7.90x10^4$), 360 nm ($6.82x10^4$), 260 nm ($7.54x10^4$) and 233 nm ($6.10x10^4$).

(xiii) 2-Methyleneanthraquinonyltriphenylphosphonium bromide (13) :-

1.50 g of 2-bromomethylanthraquinone (5.00×10^{-3} mole), 1.5 g of triphenylphosphine (5.72×10^{-3} mole) were dissolved in 20 ml of benzene in 100 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (90%) (lit[74] 88%). Melting point 312-315 °C. (lit[74] 320 °C). IR spectrum revealed the CO stretch 1674 (lit[74] 1676) cm^{-1}. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.8 (2H, d, J= 13.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 328 nm ($0.53x10^4$), 259 nm ($8.76x10^4$) and 233 nm ($7.66x10^4$).

(xiv) 2-Methyleneanthraquinonyltriphenylphosphonium hexafluoroantimonate (14):-

1.09 g of 2-Methyleneanthraquinonyltriphenylphosphonium bromide (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (98%). Melting point 243-244.5 °C. IR spectrum revealed the CO stretch 1670

cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.6 (2H, d, J= 14.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 327 nm ($0.62x10^5$), 272 nm ($1.99x10^5$), 266 nm ($3.16x10^5$), 258 nm ($5.75x10^5$) and 229 nm ($3.41x10^5$).

(xv) Benzyltriphenylphosphonium chloride (15) :-

2.53 g of bezylchloride (2.00×10^{-2} mole), 5.5 g of triphenylphosphine (2.10×10^{-2} mole) were dissolved in 40 ml of chloroform in 75 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was stirred for 3.5 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (30%) (lit.[75] 100%). Melting point 324-327 °C (lit.[75] 317-318 °C). ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.6 (2H, d, J= 14.7 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm ($4.39x10^4$), 269 nm ($5.49x10^4$), 235 nm ($8.19x10^4$) and 233 nm ($7.60x10^4$).

(xvi) p-Nitrobenzyltriphenylphosphonium bromide (16) :-

3.45 g of p-nitrobenzylbromide (2.00×10^{-2} mole), 5.5 g of triphenylphosphine (2.10×10^{-2} mole) were dissolved in 60 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (96%). Melting point

270-271 °C. IR spectrum revealed the NO_2 stretch 1350 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.0 (2H, d, J= 14.4 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm ($1.61x10^5$), 269 nm ($1.75x10^5$), 262 nm ($1.61x10^5$) and 228 nm ($3.04x10^5$).

(xvii) p-Nitrobenzyltriphenylphosphonium hexaflouroantimonate (17) :-

2.17 g of p-Nitrobenzyltriphenylphosphonium bromide (5.00×10^{-3} Mole), 1.5 g of $KSbF_6$ (5.45×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (98%). Melting point 173-173.5 °C. IR spectrum revealed the NO_2 stretch 1350 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.2 (2H, d, J= 14.4 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm (3.04x105), 268 nm ($3.51x10^5$), 264 nm (3.35x10su5) and 231 nm ($5.80x10^5$) respectively in dichloromethane.

(xviii) p-Bromobenzyltriphenylphosphonium bromide (18) :-

2.50 g of p-Bromobenzyltriphenylphosphonium bromide (1.00×10^{-2} mole), 2.8 g of triphenylphosphine (1.06×10^{-2} mole) were dissolved in 40 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (97%). Melting point 267-268 °C (lit.[76] 278 °C).

^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.6 (2H, d, J= 14.4 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275 nm ($4.28x10^4$), 268.3 nm ($1.46x10^4$), 261.8 nm ($1.04x10^4$), 236 nm ($0.70x10^4$) and 231 nm ($0.99x10^4$).

(xix) p-Bromobenzyltriphenylphosphonium hexaflouroantimonate (19) :-

1.28 g of p-Bromobenzyltriphenylphosphonium bromide (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (98%). Melting point 155-159 °C. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.9 (2H, d, J= 14.4 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275.68 nm ($3.92x10^4$), 268.63 nm ($4.70x10^4$) and 229 nm ($1.57x10^4$).

(xx) p,p'-Bis (methylenetriphenylphosphonium chloride) benzene (20) :-

3.50 g of α,α'-Dichloro-p-xylene (2.00×10^{-2} mole), 5.5 g of triphenylphosphine (2.10×10^{-2} mole) were dissolved in 75 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (86%). Melting point 270-275 °C. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.5 (2H, d, J= 13.1 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in

dichloromethane : 275.3 nm ($6.90x10^4$), 268.3 nm ($8.7x10^4$) and 236 nm ($9.20x10^4$).

(xxi) Poly (metylenetriphenylphosphonium chloride) styrene (21) :-

5.0 ml of chloromethylstyrene was heated with 0.005 g of benzoyl peroxide in three necked flask on water bath at 70°C for 4 h. A viscous material was formed which was poured in methanol for precipitation. The precipitate formed was filtered and dried under vacuum. Further purification was done by dissolving it in dichloromethane and pouring it into methanol. 1.6 g of this polychloromethylstyrene formed was refluxed with 3.0 g of triphenyl phosphine in 40 ml of dry benzene for eight hours. A sticky material was formed which was precipitated in cyclohexane. It was filtered and dried under vacuum. percentage yield was found to be 73%. Melting point was not clear but decomposition starts at 172 °C as colour of the salt changed at this temperature. It became darker if further heated. Colour changed to dark violet after 320 °C and even after 350 °C melting point was not found. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 2.2 (2H, d, J= 14.5 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 272.71 nm ($1.71x10^3$), 260 nm ($1.93x10^3$) and 228 nm ($2.23x10^3$).

(xxii) Poly (p-metylenetriphenylphosphonium hexafluoroantimonate) styrene (22) :-

1.03 g of Poly (metylenetriphenylphosphoniumchloride) styrene, 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for two hours. The solvent used was 50/50 mixture of water/methanol by volume, The salt was recovered as mentioned in the general procedure. Melting point 172 °C (decomposition) as colour of the salt changed at this temperature. It became darker

if further heated. Colour changed to dark violet after 320 °C and even after 350 °C melting point was not found. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 2.4 (2H, d, J= 13.8 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 275.68 nm ($2.13x10^3$), 268 nm ($2.61x10^3$), 263 nm ($2.36x10^3$) and 232 nm ($14.37x10^3$).

(2) Phosphonium ylids

Phosphonium ylids were prepared by continuous stirring of the corresponding phosphonium bromide or chloride salts with excess of aqueous sodium hydroxide for two hours. They were washed with water several times to remove the base. It was dissolved in dichloromethane and dried over calcium chloride. The solvent was removed by rotavap and the ylid was dried under vacuum. Further purification was done by dissolving in chloroform and precipitating out by diethyl ether.

(i) Phenacyltriphenylphosphonium ylid (23) :-

Prepared and recovered by the general method as in synthesis of phosphonium ylid (98%). Melting point 184-184.5 °C (lit.[72] 183-184 °C). IR spectrum revealed the CO stretch 1525 cm^{-1}. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.6 (1H, d, J= 24.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 327 nm ($1.18x10^4$), 241 nm ($1.80x10^4$), 237 nm ($2.26x10^4$), 236 nm ($2.40x10^4$) and 233 nm ($2.76x10^4$).

(ii) p-Bromophenacyltriphenylphosphonium ylid (24) :-

Prepared and recovered by the general method as in synthesis of phosphonium ylid (95%). Melting point 189-190.5 °C (lit.[77] 199-201 °C). IR spectrum revealed the CO stretch 1577 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.6 (1H, d, J= 24.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 331 nm ($1.79x10^4$) and 231 nm ($1.47x10^4$).

(iii) Acetonyltriphenylphosphonium ylid (25) :-

Prepared and recovered by the general method as in synthesis of phosphonium ylid (96%). Melting point 205-206.5 °C (lit.[72] 205-206°C). IR spectrum revealed the CO stretch 1587 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 3.7 (1H, d, J= 27.0 Hz). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 232 nm ($7.80x10^3$).

(3) *Arsonium salts*

All the arsonium salts were synthesized by refluxing equimolar amount of their respective bromides or chlorides, mentioned in the starting materials, and triphenylarsine in benzene for four hours to twelve hours except benzyltriphenylarsonium chloride where the solvent used was chloroform and it was stirred at room temperature and was recovered by crystalization in ethanol. In the other salts mixture was refluxed in benzene and the salt was recovered by keeping the refluxed material overnight at room temperature. Further purification was done either by precipitation of chloroform solution in diethyl ether or hexane or by

recrystallization in benzene.

The anions of arsonium salts formed were replaced by reaction of the bromide or chloride salts with KPF_6 or $KSbF_6$ as described in the synthesis of phosphonium salt.

(i) Phenacyltriphenylarsonium bromide (26) :-

5.97 g of phenacylbromide (3.00×10^{-2} mole), 10.0 g of triphenylarsine (3.27×10^{-2} mole) were dissolved in 100 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (67%). Melting point 184-186 °C (lit.[78] 182-183 and lit[73] 186 °C). IR spectrum revealed the CO stretch 1652 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.5 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 255 nm (1.77×10^4), 238 nm (1.18×10^4) and 230 nm (1.8×10^4).

(ii) Phenacyltriphenylarsonium hexafluoroantimonate (27) :-

1.26 g of Phenacyltriphenylarsonium bromide (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (89%). Melting point 120-122 °C. IR spectrum revealed the CO stretch 1679 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.4 (2H, s). UV spectrum has following absorption

maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 258 nm ($2.15x10^4$) and 230 nm ($1.81x10^4$).

(iii) Phenacyltriphenylarsonium hexafluorophosphate (28) :-

1.26 g of phenacyltriphenylphosphonium bromide (2.50×10^{-3} Mole), 0.6 g of KPF_6 (3.26×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (92%). Melting point 160-161 °C. IR spectrum revealed the CO stretch 1653 & 1674 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.0 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 256 nm ($2.32x10^4$), 230 nm ($2.32x10^4$) and 229 nm ($2.37x10^4$).

(iv) p-Bromophenacyltriphenylarsonium bromide (29) :-

5.56 g of p-Bromophenacylbromide (2.00×10^{-2} mole), 6.5 g of triphenylarsine (2.12×10^{-2} mole) were dissolved in 80 ml of benzene in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (78%). Melting point 155-156 °C. (lit.[73] 158 °C). IR spectrum revealed the CO stretch 1666 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 6.3 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 271 nm ($2.29x10^5$), 265.29 nm ($2.18x10^4$) and 228 nm ($2.02x10^4$).

(v) p-Bromophenacyltriphenylarsonium hexafluoroantimonate (30) :-

1.46 g of p-Bromophenacyltriphenylarsonium bromide (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (88%). Melting point 186-187 °C. IR spectrum revealed the CO stretch 1678 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.4 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : at 272 nm (2.79×10^4), 265.29 nm (2.37×10^4), 228 nm and (2.11×10^4).

(vi) p-Bromophenacyltriphenylarsonium hexafluorophosphate (31) :-

1.426 g of p-Bromophenacyltriphenylphosphonium bromide (2.50×10^{-3} Mole), 0.6 g of KPF_6 (3.26×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (91%). Melting point 201.5-202 °C. IR spectrum revealed the CO stretch at 1677 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.3 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 272 nm (2.75×10^4), 265.66 nm (2.37×10^4) and 228 nm (2.14×10^4).

(vii) 9-Methyleneanthracenyltriphenylarsonium chloride (32) :-

1.13 g of 9-chloromethyl anthracene (5.00×10^{-3} mole), 1.60 g of triphenylarsine

(5.27×10^{-3} mole) were dissolved in 20 ml of benzene in 100 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (46%). Melting point 134-136 °C. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 7.5 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 392 nm (2.07×10^4), 372 nm (2.34×10^4), 358 nm (1.69×10^4), 258 nm (3.75×10^4), and 225 nm (2.28×10^4).

(viii) 9-Methyleneanthracenyltriphenylarsoniumhexafluoroantimonate (33) :-

1.33 g of 9-Methyleneanthracenyltriphenylarsonium chloride (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (89%). Melting point 132-136 °C. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.6 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 391 nm (1.88×10^4), 371 nm (2.19×10^4), 260 nm (8.37×10^4), 353 nm (1.62×10^4), 235 nm (3.93×10^4) and 225 nm (2.00×10^4).

(ix) 2-Methyleneanthraquinonyltriphenylarsonium bromide (34) :-

1.15 g of 2-Bromomethylanthraquinone (5.00×10^{-3} mole), 10.0 g of triphenylarsine (5.23×10^{-3} mole) were dissolved in 20 ml of benzene in 100 ml

round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was refluxed for 4 h. After that time the mixture was cooled to room temperature. The salt was recovered as mentioned in the general procedure (49%). Melting point 194-197 °C. IR spectrum revealed the CO stretch 1670 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.7 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 328 nm ($1.28x10^4$), 277.54 nm (32880), 258 nm and ($9.40x10^{4)}$

(x) 2-Methyleneanthraquinonyltriphenylarsonium hexafluoroantimonate (35) :-

1.20 g of 2-Methyleneanthraquinonyltriphenylarsonium bromide (2.50×10^{-3} Mole), 0.85 g of $KSbF_6$ (3.09×10^{-3} mole) were stirred in 100 ml of solvent for 2 h. The solvent used was 50/50 mixture of water/methanol by volume. The salt was recovered as mentioned in the general procedure (96%). Melting point 197-198.5 °C. IR spectrum revealed the CO stretch 1670 cm^{-1}. ^1H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 4.7 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 328 nm ($1.78x10^4$), 277.59 nm ($4.84x10^4$) and 258 nm ($1.40x10^4$)

(xi) Benzyltriphenylarsonium chloride (36):-

1.27 g of bezylchloride (1.00×10^{-2} mole), 3.3 g of triphenylarsine (1.24×10^{-2} mole) were dissolved in 40 ml of chloroform in 250 ml round bottomed flask equiped with a teflon coated magnetic stirring bar and a reflux condenser. The reaction mixture was stirred for 5 h. After that time the mixture was cooled to

room temperature. The salt was recovered by addition of excess of diethylether (57%). Melting point 60-61.5 °C. ^{1}H NMR ($CDCl_3$) spectrum displayed CH_2 signal at δ 5.6 (2H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 249 nm ($1.76x10^4$) and 229 nm ($1.54x10^4$).

(2) *Arsonium ylids*

(i) Phenacyltriphenylarsonium ylid :-

Phenacyltriphenylarsonium ylid was prepared by continuous stirring of pheacyltriphenylarsonium bromide salts with excess of aqueous sodium hydroxide for 2 h. It was washed with water several times to remove the base. It was dissolved in dichloromethane and was dried over calcium chloride and the solvent was removed by rotavap. The ylid was dried under vacuum. For further purification it was dissolved in small amount of dichloromethane and filtered over calcium chloride to remove moisture and it was precipitated by ether(77%). Melting point 153.5-155 °C. IR spectrum revealed the CO stretch 1652 cm^{-1}. ^{1}H NMR ($CDCl_3$) spectrum displayed CH signal at delta 4.7 (1H, s). UV spectrum has following absorption maxima λ_{max} and extinction coefficients ε_{max} (written in parenthesis) in dichloromethane : 328 nm ($1.07x10^4$), 265 nm ($4.63x10^4$) and 234 nm ($1.81x10^4$).

2.5 High Vacuum Apparatus

A pyrex high vacuum line was constructed as shown in figure (2.1) The line was connected to a pumping system which consist Bendix VMF type diffusion pump backed by mechanical pump. Ther were two liquid nitrogen cold traps of which only one was used because the diffusion pump was built in with the mechanical pump. The cooling system for the diffusion pump was LAUDA K-4/R model of Brinkmann Instruments. The vacuum obtained was monitored by thermocouple vacuum gauge Varian Modle 804-A. First mechanical pump was turned on. When the system pressure .5 torr or less, the cooling system and VMF pump heater was turned on.

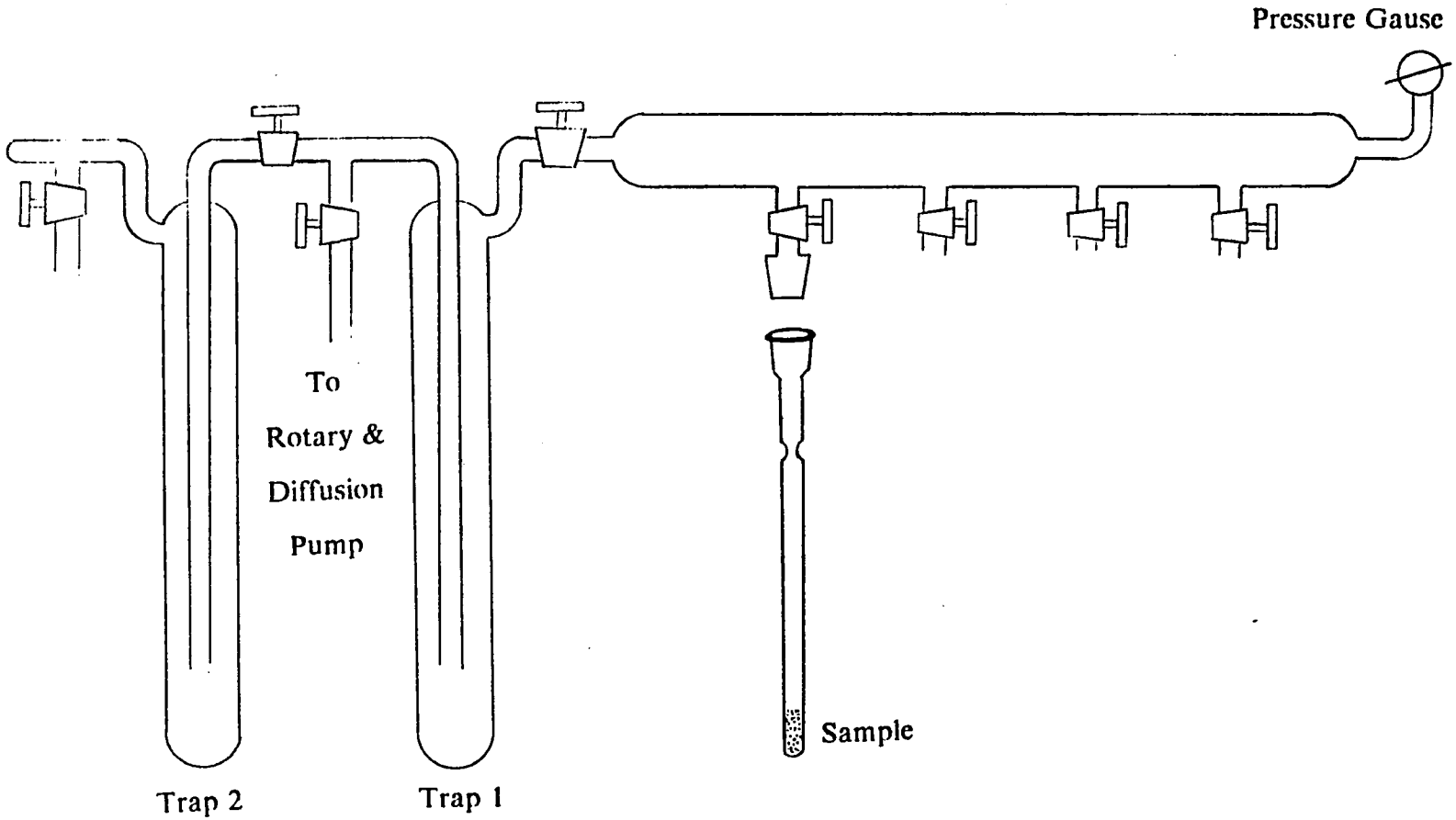


Figure 2.1 : Vacuum line used for degassing the sample

2.6 Source of Radiation

Tow radiation sources were used. Major part of work was covered by using Xenon Arc Lamp of Varian. Illuminator power supply was controlled by model PS 150-8 of Varian and the radiation source used was model PSW 2107 FL from Varian. The lamp was calibrated (in R.I., KFUPM) by comparison with the MSL reference standard of spectral irradiance having calibration traceable to the National Bureau of Standard USA. The lamp was used at two different current values of 8 amp. and 12 amp. Their values are given in table (2.1).

Data analysis was done from 300 nm to 345 nm. Irradiance and photon irradiance for 12 Amps. current were 6.989 microwatts cm^{-2} and $1.158x10^{14}$ photons $Sec.^{-1}cm^{-2}$ respectively and those for 8 Amps current were 6.308 mi crowatts cm^{-2} and $1.048x10^{14}$ photons $Sec.^{-1}cm^{-2}$. Their calibration values are given in table (2.2)

***Table* (2.1** Irradiation used at different output current.

Current (A)	**total Irradiance** $\mu W/cm^2$	**Photon Irradiance (Photons/sec** cm^2	**Illuminance Lux (lm/** m^2)
8	$2.238X\ 10^5$	$7.084\ X\ 10^{17}$	$4.979\ X\ 10^5$
12	$3.554\ X\ 10^5$	$1.124\ X\ 10^{18}$	$7.958\ X\ 10^5$

***Table* (2.3)** Calibration values of lamp used.

8 Amps.		**12 Amps.**	
W.L. (nm)	Value Microwatts $cm^{-2}nm^{-1}$	W.L. (nm)	Value Microwatts $cm^{-2}nm^{-1}$
300.0	$2.1345x10^{-1}$	300.0	$2.1920x10^{-1}$
305.0	$4.1792x10^{-1}$	305.0	$4.2960x10^{-1}$
310.0	$2.0743x10^{0}$	310.0	$2.6468x10^{0}$
315.0	$9.9167x10^{-1}$	315.0	$1.1772x10^{0}$
320.0	$9.3973x10^{-1}$	320.0	$1.0796x10^{0}$
325.0	$1.0530x10^{0}$	325.0	$1.1832x10^{0}$
330.0	$1.2071x10^{0}$	330.0	$1.3548x10^{0}$
335.0	$1.4699x10^{0}$	335.0	$1.5680x10^{0}$
340.0	$1.7416x10^{0}$	340.0	$1.8012x10^{0}$
345.0	$1.9607x10^{0}$	345.0	$2.0448x10^{0}$

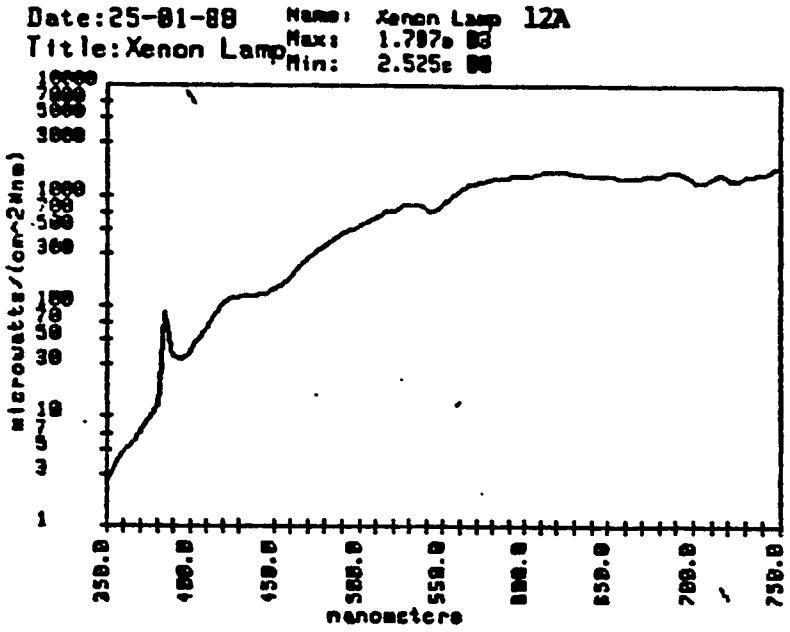


Figure 2.2 : Calibration curve at 12 amp. output current.

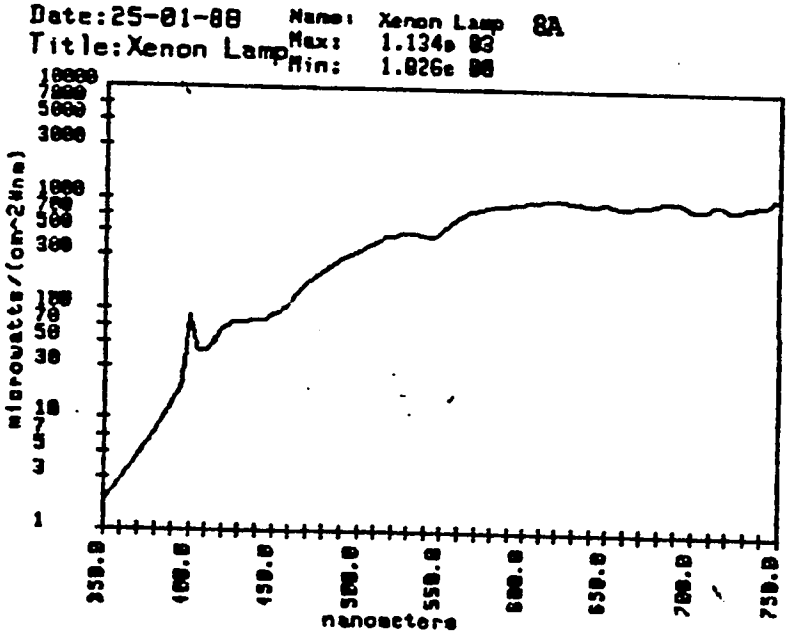


Figure 2.3 : Calibration curve at 8 amp. output current.

Another ultraviolet lamp used was model B-100A of THOMAS Scientific for 366nm radiation. This light source is a high pressure mercury vapour bulb, 100 watt, sealed beam, spot type. The bulb in this apparatus has a intensity of 1020 v W/cm^2 at 15 inches.

2.7 Analytical Instruments

(i) Infrared Spectroscopy (IR) :-

Infrared spectra were recorded on Nicolet 5 DXB FTIR spectrometer using KBr disk of the samples.

(ii) Nuclear Magnetic Resonance Spectroscopy (NMR) :-

^{1}H NMR spectra were taken on Bruker AC 80 NMR spectrometer and ^{31}P NMR spectra were taken on XL-200 Multineuclear NMR spectrometer using deuterated chloroform or deuterated DMSO as solvent with tetramethyl silane as external standard.

(iii) Ultraviolet-Visible Spectroscopy (UV-VIS) :-

A Varian Cary Model 2390 UV-VIS-NIR Spectrometer was used for all ultraviolet visible spectra. For recording spectra a precision quartz cell of path length 1 cm was used. Extinction coefficients were calculated by using the equation

$$A = \varepsilon CL$$

for the solution of known concentration.

(iv) Elemental analysis :-

Elemental analysis were performed on a Carlo-Erba Model 1106 Elemental analyzer for carbon, hydrogen and nitrogen.

(v) Molecular weight determination :-

Molecular weight of polymers was obtained by using Waters 150-C ALC/GPC, a type of liquid-solid elution chromatography which seperates polydisperse polymers into fractions by means of the sieving action of a cross-linked polystyrene gel. The polymer fractions are seperated on the basis of polymer size because the elution of highest molecular weight fractions happens first. Some of the operating conditions and experimental details of the instrument used are given below :

Column Type	Ultrastyragel
Column exclusion limits	500, 10^3, 10^4, and 10^5 ^{0}A
Flow rate	1 ml/minute
Solution concentration	0.125% mass/volume (m/v)
Sample size	50 µl
Operating temperature	30 °C
Sample solution preparation	Allowed to stand overnight at 35 °C, filtered through stainless steel filter (0.5 micron) prior to injection.

2.8 Polymerization method

The required amount of monomer and initiators and/or any other adduct in dichloromethane were pippeted into Pyrex tube of 12 mm diameter constructed as

shown in figure 2.1 and these were rapidly transfered to the high vacuum line and pumped out. The tubes were surrounded at their bases with a liquid nitrogen coolant and the whole was pumped till vacuum 10^{-4} was reached. This usual freeze and thaw method was repeated three times then the tube was sealed off at the constriction whilst still under vacuum. After the seal off point had cooled, the tube was subjected to thermal (50 °C or 70 °C) or photochemical processes (25 °C), as the case might be. When the required time period had elapsed the tube was removed, dried and hot spotted open on a line made in the tube with a glass knife. The polymer was then recovered as explained in section 2.10.

2.9 Measurements of Rate of Polymerization

Polymerizations were carried out as described above. The rate of polymerization were determined gravimetrically from the following expression.

$$R_p = \frac{w}{m} \times \frac{1000}{v} \times \frac{1}{t}$$

where,

m = monomer molecular weight

w = weight of polymers (g)

v = volume of solution in reaction mixture

t = polymerization time (sec.)

This expression can be simplified as

$$R_p = \text{Percent Conversion} \times \frac{10}{m.t.d}$$

Where d = density of monomer

2.10 Polymer Recovery

After the polymerization the polymer was precipitated by the addition of an excess of methanol containing a few drops of dilute HCl, washed with methanol and dried under vacuum. The polymer resulting was a white solid which was purified by repeated reprecipitation from dichloromethane / methanol system.

(i) Polycyclohexene oxide :-

The yield of polymer was calculated on the basis of 100 % theoretical yield being 971 g polycyclohexene oxide from one litre of monomer at 25 °C.

(ii) Polystyrene :-

The yield of polymer was calculated on the basis of 100 % theoretical yield being 906 g polystyrene from one litre of monomer at 25 °C.

(iii) Poly p-methyl styrene :-

The yield of polymer was calculated on the basis of 100 % theoretical yield being 897 g poly p-methyl styrene from one litre of monomer at 25 °C.

(iv) Polymethylmethacrylate :-

The yield of polymer was calculated on the basis of 100 % theoretical yield being 936 g polymethylmethacrylate from one litre of monomer at 25 °C.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 PROPERTIES OF PHOSPHONIUM SALTS :-

All phosphonium salts are stable under laboratory conditions. They are white or slightly yellow crystalline solid . Phosphonium salts of 9-chloromethyl anthracene is yellow and that of 2-bromomethyl anthraquinone is light yellow. They are all soluble in dichloromethane, chloroform, acetone, THF, dioxane and partially soluble in ethanol and methanol. p-Bromophenacyltriphenyl phosphonium and arsonium salts are less soluble in chloroform than the others. All of them are insoluble in water. Their physical properties are shown in table (3.1)

3.2 PROPERTIES OF PHOSPHONIUM YLIDS :-

All the four phosphonium ylids we used, are white in colour and crystalline in nature. All of them are stable under the laboratory conditions. They are all soluble in dichloromethane, chloroform, acetone, THF, dioxane and partially soluble in ethanol and methanol. They are insoluble in water. Their physical and spectral parameters are outlined in table (3.2).

Table (3.1) : **Properties of phosphonium salts** $R' - R - CH_2 - P^+(Ph)_3X^-$

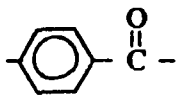
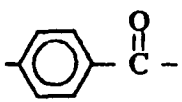
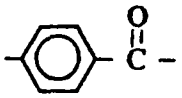
Salt No.	R′	R	X	M.P. °C	% yield	ν CO cm^{-1}	NMR δ CH_2 ppm	λ_{max} CH_2Cl_2 nm	ε_{max} CH_2Cl_2 $M^{-1}cm^{-1}$
1	H		Br	274-76	92.39	1660	6.5	254 235 234 232 231	880000 332000 350000 800000 390000
2	H		SbF_6	144-46	82.10	1687	5.6	257 234 232	32270 44024 64980
3	H		PF_6	170-71	91.80	1682	5.3	257 236 230	25600 29800 37000

Table (3.1) contd.....

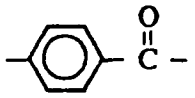
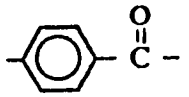
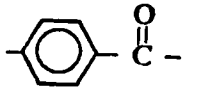
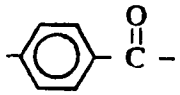
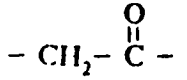
4	Br		Br	222-24	91.74	1673	6.4	269 229	6200 39960
5	Br		SbF_6	166.5-68	83.20	1677	5.3	275 257 229	41100 22260 46260
6	Br		PF_6	209-09.5	81.50	1677	6.2	275 269 229	38500 37820 40700
7	Ph		Br	125-25.5	57.00	1680.7	6.4	305 309 235	270800 26440 322800
8	H		Cl	243.70	-----	1680	5.6	273 267 258 229	56000 67520 67520 319220

Table (3.1) contd.....

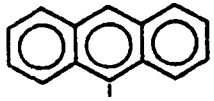
9	H	$-CH_2-\overset{O}{\overset{\|}{\underset{\|}{C}}}-$	SbF_6	154-55	97.80	1700	4.7	275 268 235	87000 88000 84000
10	H	$-CH_2-\overset{O}{\overset{\|}{\underset{\|}{C}}}-$	PF_6	160-61	98.30	1728	4.8	275 268 251 235	28132 34018 10772 91000
11	H		Cl	285-86	61.33	----	6.5	400 380 375 360 315 260 255 235	73450 74202 73454 60780 34936 71984 71428 62148

Table (3.1) contd.....

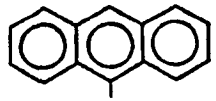
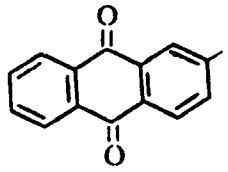
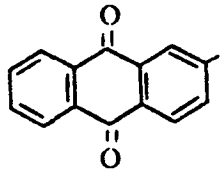
12	H		SbF_6	246-47	95.50	----	5.8	400 380 360 260 233	78180 79010 68208 75410 60984
13	H		Br	312-15	90.50	1674	5.9	328 259 233	53450 87576 76584
14	H		SbF_6	243-44.5	98.71	1670	4.6	327 272 266 258 229	61760 199280 315560 575200 341260

Table (3.1) contd.....

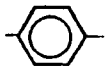
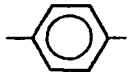
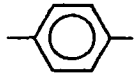
15	H		Cl	324-27	29.49	----	5.6	275 269 235 233	43922 54914 81888 76024
16	NO_2		Br	270-71	96.98	----	6.1	275 269 262 228	160520 175810 160520 303780
17	NO_2		SbF_6	173-73.5	98.71	----	4.8	275 268 264 231	303920 351420 334920 580300
18	Br		Br	257-58	97.56	----	5.6	275 268.3 262 236 231	42848 14634 10358 7000 9888

Table (3.1) contd.....

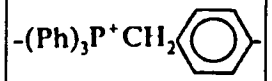
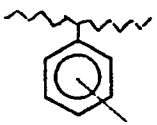
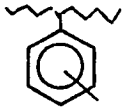
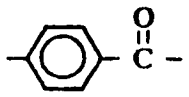
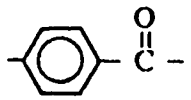
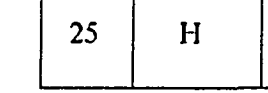
19	Br		SbF_6	155-59	98.50	----	4.8	275.68 268.63 229	39180 46980 156540
20	Br		Br	270-75	86.19	----	5.6	275.3 268.3 236	68984 87000 92000
21	H		Br	320-50	48.50	----	2.2	272.7 260 228	1712 1932 2225.8
22	H		SbF_6	320-50	78.50	----	2.1	275.68 268 263 232	2125.2 2610 2358 14372

Table (3.2) : **Properties of phosphonium ylids R′ – R – CH = P(Ph)$_3$**

Salt No.	R′	R	M.P. °C	% yield	ν CO cm^{-1}	NMR δ CH ppm	λ_{max} CH_2Cl_2 nm	ε_{max} CH_2Cl_2 $M^{-1}cm^{-1}$
23	H		184-84.5	98.50	1516	4.5	327 241 237 236 233 230	11820 17990 22640 23968 27584 29230
24	Br		189-90.5	95.00	1519	4.4	255 231	17655.6 14676
25	H		205-06.5	96.50	1587	3.8	232	7796.4

3.3 PROPERTIES OF ARSONIUM SALTS :-

Arsonium salt of 9-chloromethyl anthracene was of cream colour but with yellow shed and that of 2-bromomethyl anthraquinone was of dirty cream colour. All other arsonium salts were good crystals of white colour. They were all stable under laboratory condition and were soluble in dichloromethane, chloroform, acetone, THF, dioxane and partially soluble in ethanol and methanol. They are insoluble in water. Their physical and spectral parameters are given in table (3.3).

3.4 PROPERTIES OF ARSONIUM YLIDS :-

Only one arsonium ylid was used in our study and was white in colour, good crystals were stable under laboratory conditions. It was soluble in dichloromethane, chloroform, acetone, THF, dioxane and slightly soluble in ethanol and methanol. They are insoluble in water. Their physical and spectral parameters are outlined in table (3.4).

Table (3.3) : **Properties of arsonium salts** $R' - R - CH_2 - As^+(Ph)_3X^-$

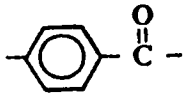
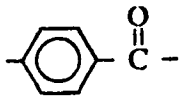
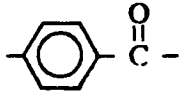
Salt No.	R′	R	X	M.P. °C	% yield	ν CO cm^{-1}	NMR δ CH_2 ppm	λ_{max} CH_2Cl_2 nm	ε_{max} CH_2Cl_2 $M^{-1}cm^{-1}$
26	H		Br	184-86	67.00	1652.7	6.52	255 238 230	17655.6 11782.8 18000
27	H		SbF_6	120-22	89.00	1660-72	5.35	258 230	21540 18000
28	H		PF_6	160-61	92.10	1653-74	6.0	256 230 229	23159 23244 23732

Table (3.3) contd.....

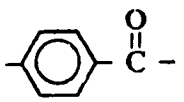
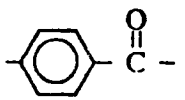
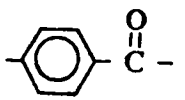
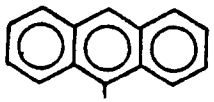
29	Br		Br	155-56	78.00	1665.5	6.26	271 265.29 228	22921 21785 20235
30	Br		SbF_6	186-87	88.00	1677.5	5.4	272 265.29 228	27587 23722 21059
31	Br		PF_6	201.5-02	91.80	1677.2	5.3	272 265.66 228	27490 23722 21429
32	H		Cl	134-36	46.90	------	6.1	392 372 358 258 225	20721.43 23350 16853.6 37484 22803.6

Table (3.3) contd.....

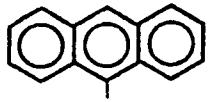
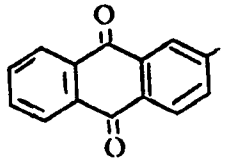
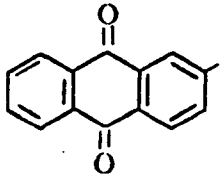
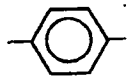
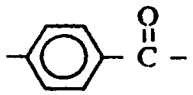
33	H		SbF_6	132-39	89.37	------	5.6	391 371 353 260 235 225	18836 21938 16150 83784 39316 19968
34	H		Br	194-97	49.56	1675	5.8	328 277.54 258	12880 32880 93972
35	H		SbF_6	197-98.5	96.13	1671	4.7	328 277.54 258	17796 48384 139752
36	H		Cl	60.5-61	57.14	------	5.62	249 229	17604 15356

Table (3.4) : **Properties of Arsonium ylids R′ − R − CH=As(Ph)$_3$**

Salt No.	R′	R	M.P. °C	% yield	ν CO cm^{-1}	NMR δ CH ppm	λ_{max} CH_2Cl_2 nm	ε_{max} CH_2Cl_2 $M^{-1}cm^{-1}$
37	H		153.5-55	77.14	1685	4.7	328 265 234	10744 4628 18114

3.5 POLYMERIZATION OF CYCLOHEXENEOXIDE :-

Cyclohexeneoxide was polymerized in this work using phosphonium and arsonium salts containing various types of chromophores. The polymerization was carried out photochemically at 25 °C and thermally in dark at 50 °C or 70 °C. The concentration of initiator was kept constant during this study ($2.75x10^{-3}M$) and that of cyclohexeneoxide was 4.95 mol/L for the purpose of comparison of the efficiency of the initiators. Solvent used was dichloromethane.

3.5.1 Photopolymerization of cyclohexeneoxide by phosphonium salts:-

Polymerization did not take place when cyclohexeneoxide and the phosphonium salt mixture were kept alone in the dark at room temperature for 24 h. There was also no polymerization when cyclohexene oxide monomer was irradiated alone for 12 h in dichloromethane medium. Exposing the monomer to light in the presence of phosphonium salt **2** or **3** X = SbF_6^- or PF_6^- resulted in the formation of polycyclohexeneoxide. Figure (3.1) shows that the formation of the polymer linearly increased with increasing irradiation time when containing fixed amount of the initiator **2** & **3**. The initial slope of these lines gives the polymerization rate. The initiation efficiency depends on the anion stability. Figure (3.1) shows that salt **3** (X = PF_6^-) gives only 25 % conversion (monomer to polymer) after 120 min and 5% after 15 min irradiation whereas salt **2** (X = SbF_6^-) gives 40% conversion after 15 min. This shows that salt **2** is about 8 times more photoactive compare to salt **3**.

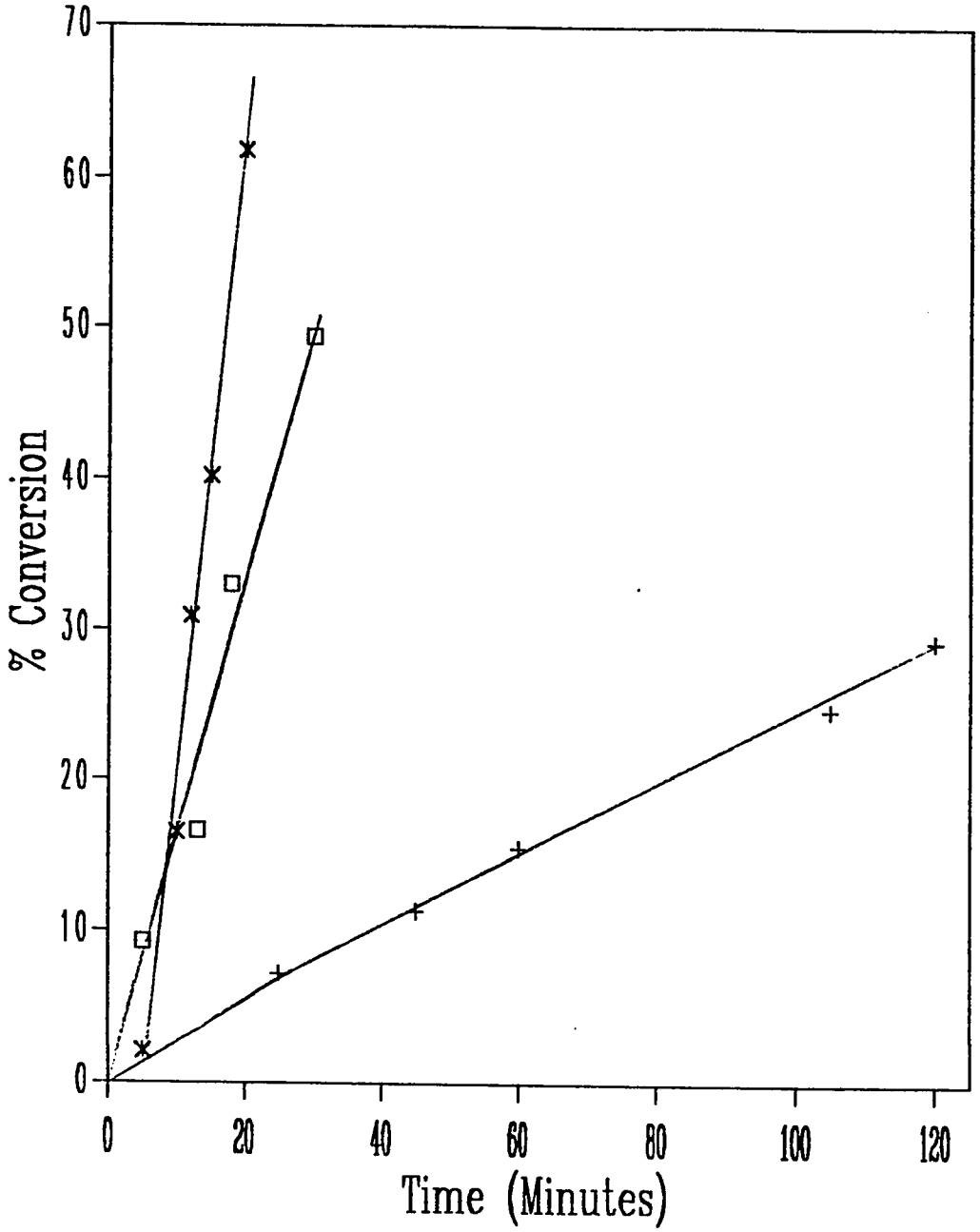
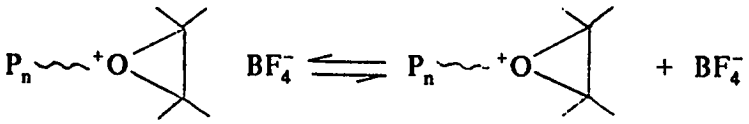
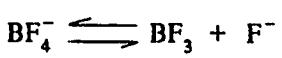
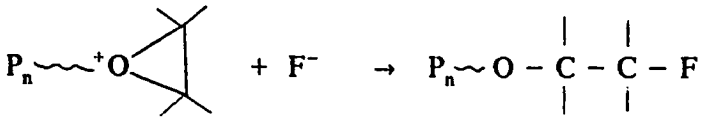


Figure 3.1 : Photopolymerization of cyclohexeneoxide by (+) initiator **3**, (□) initiator **2** (degassed), (✱) initiator **2** (not degassed). (CHO-4,5,18)

With BF_4^-, Cl^- or Br^- it was not possible to obtain any polymeric product form the reaction mixture even after long time irradiation under the same conditions. Reasonable assumption is that the cyclic oxonium ions involved in epoxide polymerization are strongly reactive towards the nucleophiles such as BF_4^-, Cl^- or Br^- as in the following (scheme 3.1).

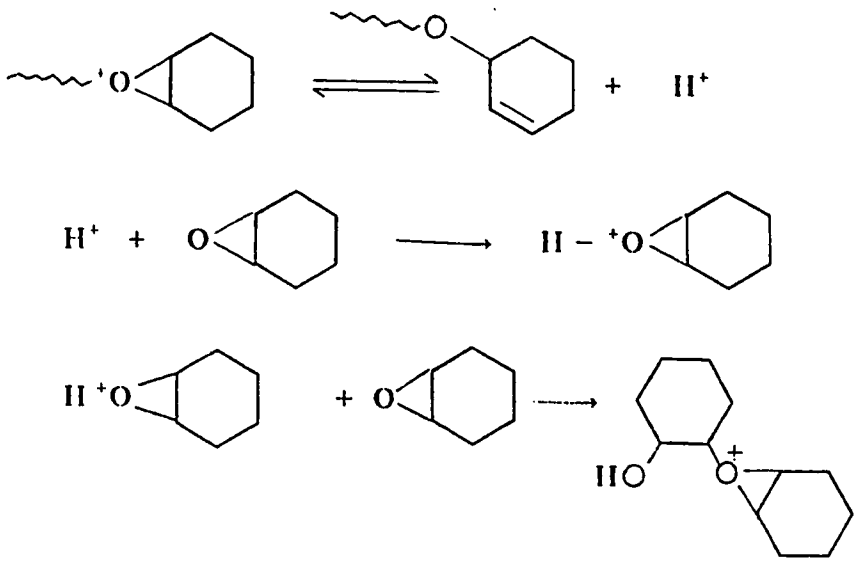






Scheme (3.1)

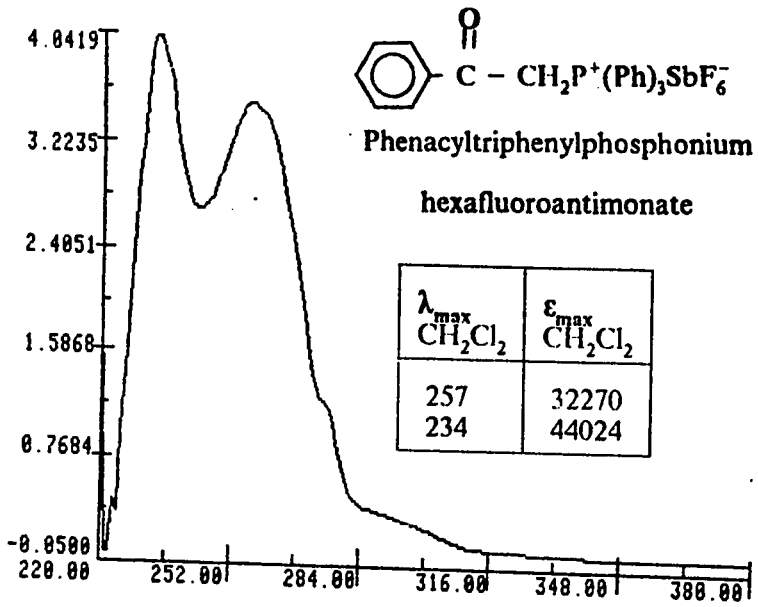
The hexafluoroantimonate anion is apparently much better at stabilizing the oxonium ion, than anion such as BF_4^-, Cl^- or Br^-. Accordingly, SbF_6^- salts should be superior initiators for cationic polymerization, possibly due to the low nucleophilicity of the SbF_6^- anion which minimizes or prevents reaction of the growing chain with the anion. This indicates that chain transfer by reaction with the poorly coordinating SbF_6^- anion which would lead to catalyst termination is not frequent. Transfer is most likely caused in these reactions as in other cationic polymerizations of vinyl ethers by transfer to monomer.[79] For epoxide polymerization the chain transfer process could be represented as in the following scheme (3.2)



etc.

Scheme (3.2)

Figure 3.1 shows that polymerization with these salts has induction period then after that the polymerization rate increase, this is more clear in case of polymerization without degassing the reaction mixture. This may be attributed at least in part to the sensitivity of epoxide polymerization to the presence of nucleophiles (such as ylid) in the presence of oxygen. Thus, substantial photolysis of the photoinitiator may be required to generate sufficient acid for "neutralization " of the nucleophiles prior to the onset of polymerization. A typical absorption spectrum of phenacyltriphenyl phosphonium salts is shown in figure (3.2). All these salts were found to have the same characteristic absorption spectrum in dichloromethane regardless of the type of the counter ion (X^-).

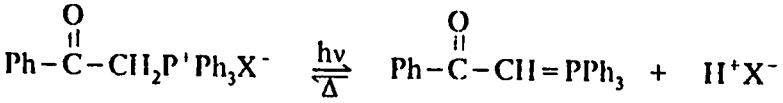


Phenacyltriphenylphosphonium hexafluoroantimonate

λ_{max} CH_2Cl_2	ε_{max} CH_2Cl_2
257	32270
234	44024

Figure 3.2 : U. V. absorption spectra of salt **2**

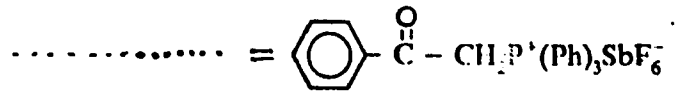
Figure 3.3 shows a comparison between the absorption spectrum of salt **2** before irradiation and after irradiation and the isolated ylid of the same salt. Since the product of photolysis H^+X^- and ylid can react reversibly to give the starting material, it is difficult here to notice any remarkable difference between these spectrum, this process can be explained as in the scheme (3.3)



Ylid (Weak base) Acid

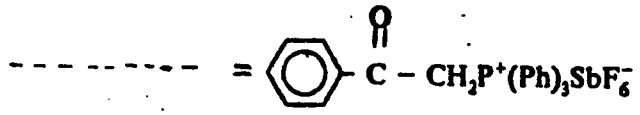
Scheme (3.3)

The NMR study (figure 3.4) also gives no change in the characteristic peaks after 8 h irradiation when compared with salt spectra before irradiation. Phenacyl phosphonium salts absorb mainly at wavelengths below 300 nm. However, photosensitization reaction of these salts by pyrene (E_T = 4.87 kcal/mol) and N-methylphenothiazine (E_T = 57 kcal/mol) makes it possible to photoinitiate cationic polymerization in the 400-500 nm reagion. Figure (3.5) demonstrated the photosensitization of these phosphonium salts by pyrene and N-methylphenothiazine. It is found that polymerization rate increases in the presence of these photosensitizers and the reaction mixture has a slight blue colour in the case of pyrene and slight pink colour in the case of N-methylphenothiazine.



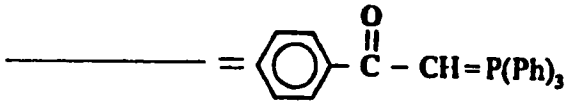
Irradiated for 3 Hours

(In Dichloromethane)



Phenacyltriphenylphosphonium

hexafluoroantimonate 2



Pheneacyltriphenylphosphonium ylid 23

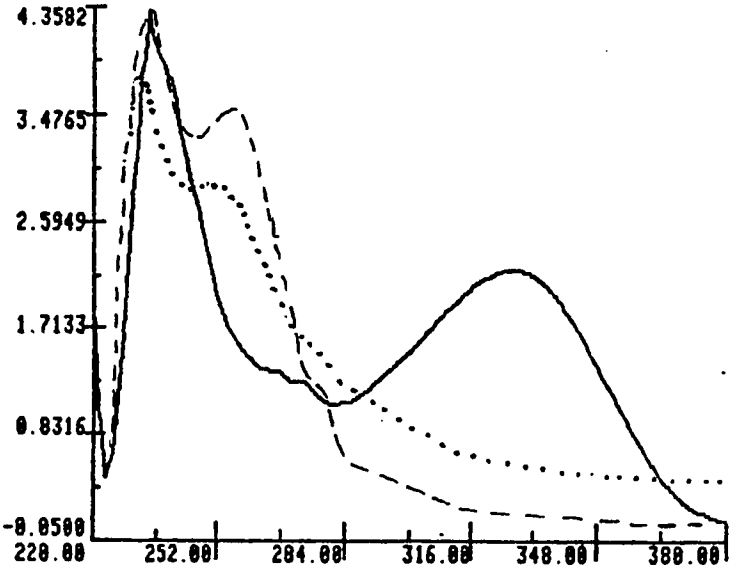


Figure 3.3 : U. V. absorption spectra of salt 2 and ylid 23.

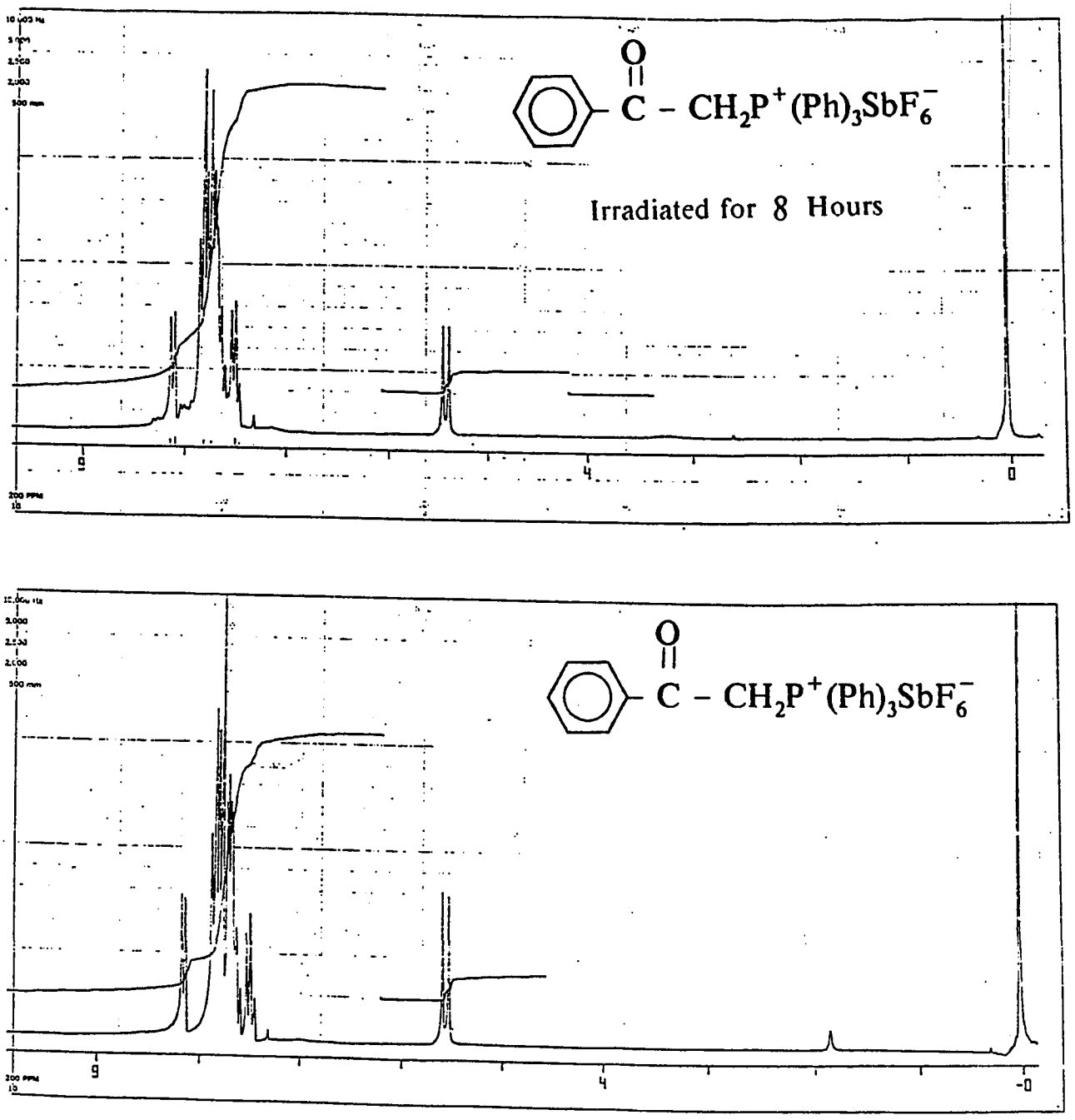


Figure 3.4 : N.M.R. spectra of salt **2** before and after irradiation.

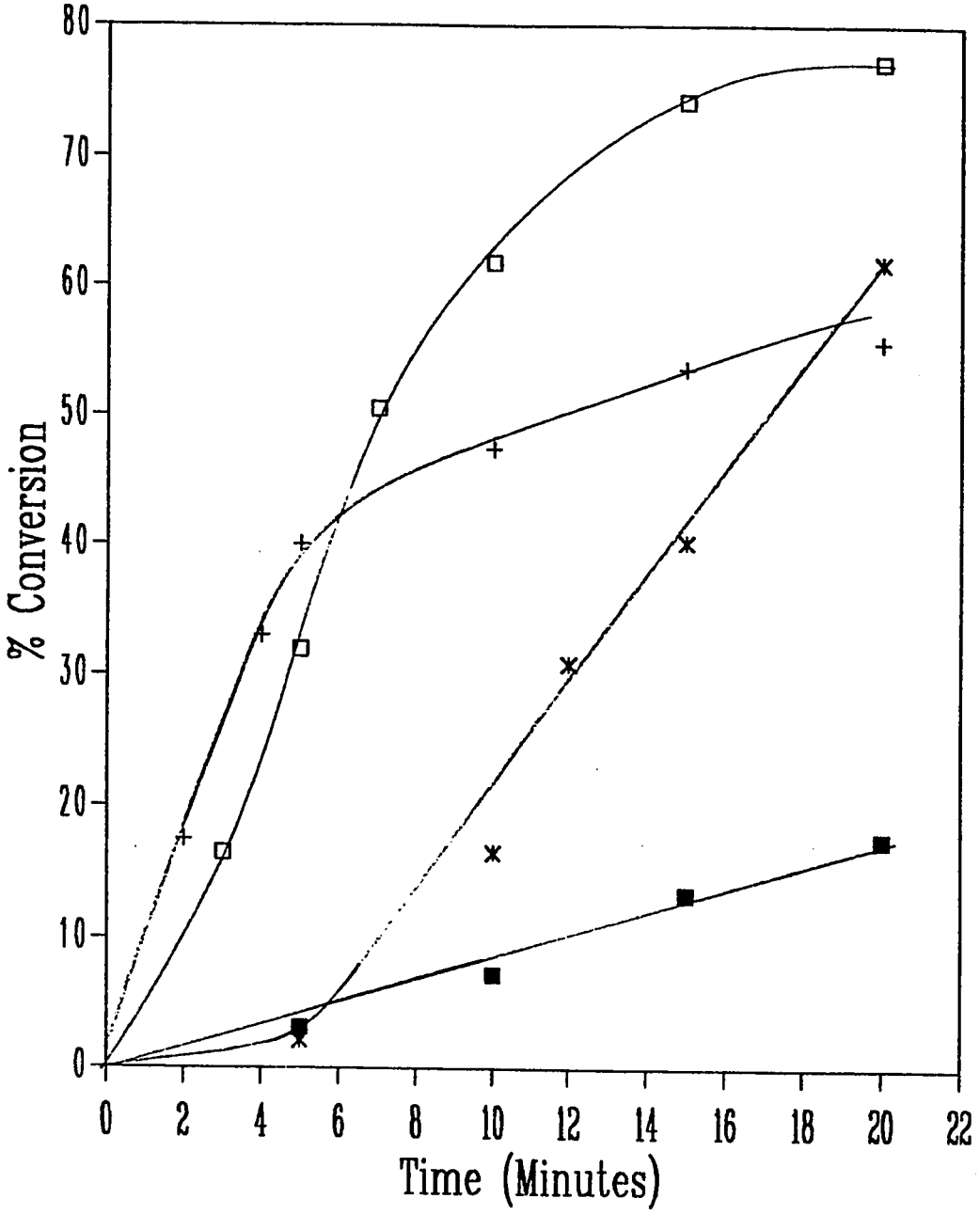
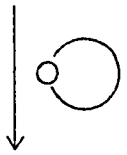


Figure 3.5 : Photopolymerization of cyclohexene oxide by (✱) initiator **2** alone, (□) initiator **2** + N-methylphenothiazine, (+) initiator **2** + pyrene, (■) initiator **2** + tis(p-bromo)phenyl amine. (CHO-3,5,6,7)

Pappas and Jilek have suggested that an exciplex is formed between the excited dye and the arylonium salt and that the exciplex decomposes chiefly by an electron transfer process.[32] Accordingly we expect that cation radical formation of phenothiazine and pyrene initiate the photopolymerization as shown in (scheme 3.4) where P = pyrene or phenothiazine

$$P \xrightarrow{h\nu} P^*$$

$$R^+X^- + P^* \rightarrow [P^*]^+ \cdot X^- + R\cdot$$



polymer

Scheme (3.4)

Less polymer was obtained when tris-(p-bromo)phenylamine was added to the monomer initiator mixture. This may be due to amine quenching of the excited phosphonium salt or the formation of amine cation radical and its decomposition in the medium before reacting with the epoxide monomer, since this produces very reactive cation radical.[80] The absorption spectrum of these photosensitizers are shown in figure (3.6 and 3.7). Figure 3.8 shows polymer obtained by adding pyrene as photosensitizer to the reaction mixture shows pyrene attached to the polymer obtained as shown in the U.V. spectra of this polymer after several precipitations.

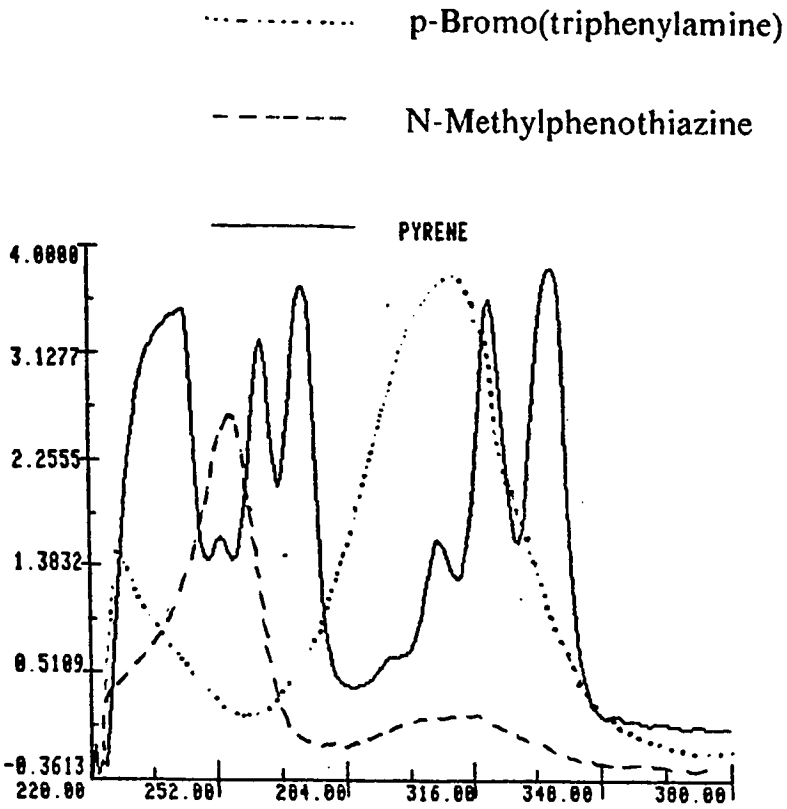


Figure 3.6 : U. V. absorption spectra of photosensitizers.

..... N-Methylphenothiazine

----- $Ph-\overset{O}{\overset{\|}{C}}-CH_2P^+(Ph)_3SbF_6^-$ 2

——— $\bigcirc-\overset{O}{\overset{\|}{C}}-CH_2P^+(Ph)_3SbF_6^-$ + N-Methylphenothiazine

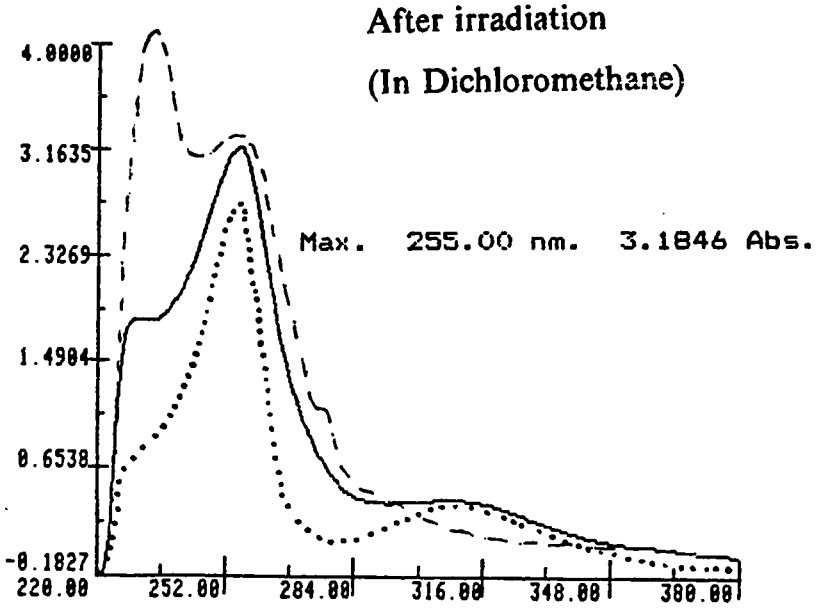


Figure 3.7 : U. V. absorption spectra of salt 2 with N-methylphenothiazine.

- - - - - = 4.95 mole/L CHO + 1.25 mole/L Pyrene

+ 1.25×10^{-3} mole/L Ph – C(=O) – $CH_2P^+(Ph)_3SbF_6^-$

(In Dichloromethane)

Irradiated for 2 Hours

——— = 4.95 mole/L CHO + 1.25 mole/L Pyrene

+ 1.25×10^{-3} mole/L Ph – C(=O) – $CH_2P^+(Ph)_3SbF_6^-$

(In Dichloromethane)

Irradiated for 15 minutes

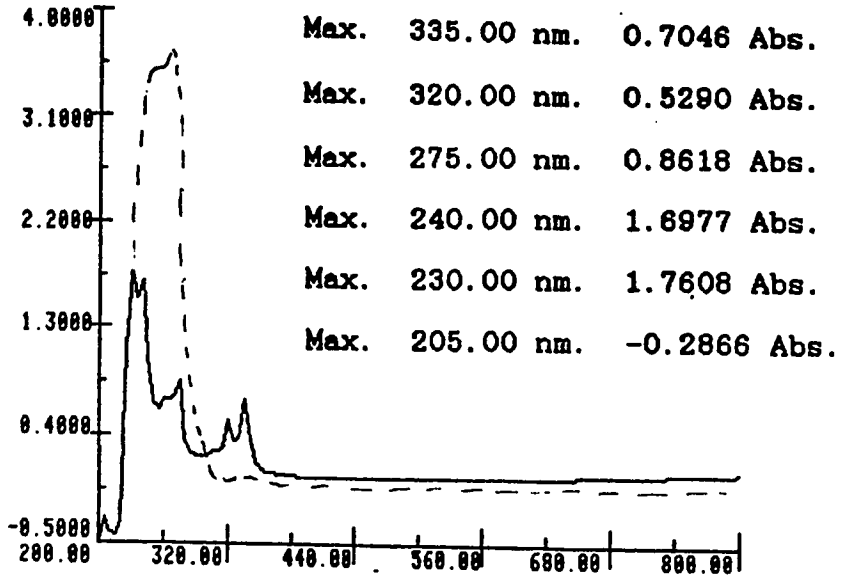


Figure 3.8 : U. V. absorption spectra of polycyclohexene oxide when pyrene was used as sesitizer.

The photopolymerization of cyclohexenoxide initiated by salt **2** (concentration $5X10^{-4}$ to $2.5X10^{-3}$mol/L) proceed as shown in figure (3.9). The rate of polymerization (Rp) is a direct function of the concentration of the salt, and the exponent value of the initiator, determined from the slope of log Rp vs log concentration of the salt. The conversion to polycyclohexene oxide can be seen to increase with the salt concentration and with irradiation time (figure 3.10 and 3.11), while the molecular weight decreases with salt concentration, Table (3.5). This is because a high salt concentration yields a large number of active centres which propagate very rapidly giving a high percentage conversion to polymer. Therefore, short polymer chains with low polymer molecular weight will be produced.

Table (3.5) **: Effect of initiator concentration on moleculer weight of poly CHO**

S.No.	Initiator conc. (Mol/L)	Irradiation time (Minutes)	Average Moleculer Weight
1	$0.5X10^{-3}$	20	25731
2	$1.0X10^{-3}$	20	24079
3	$1.5X10^{-3}$	20	18529
4	$2.0X10^{-3}$	20	18261
5	$2.5X10^{-3}$	20	14707

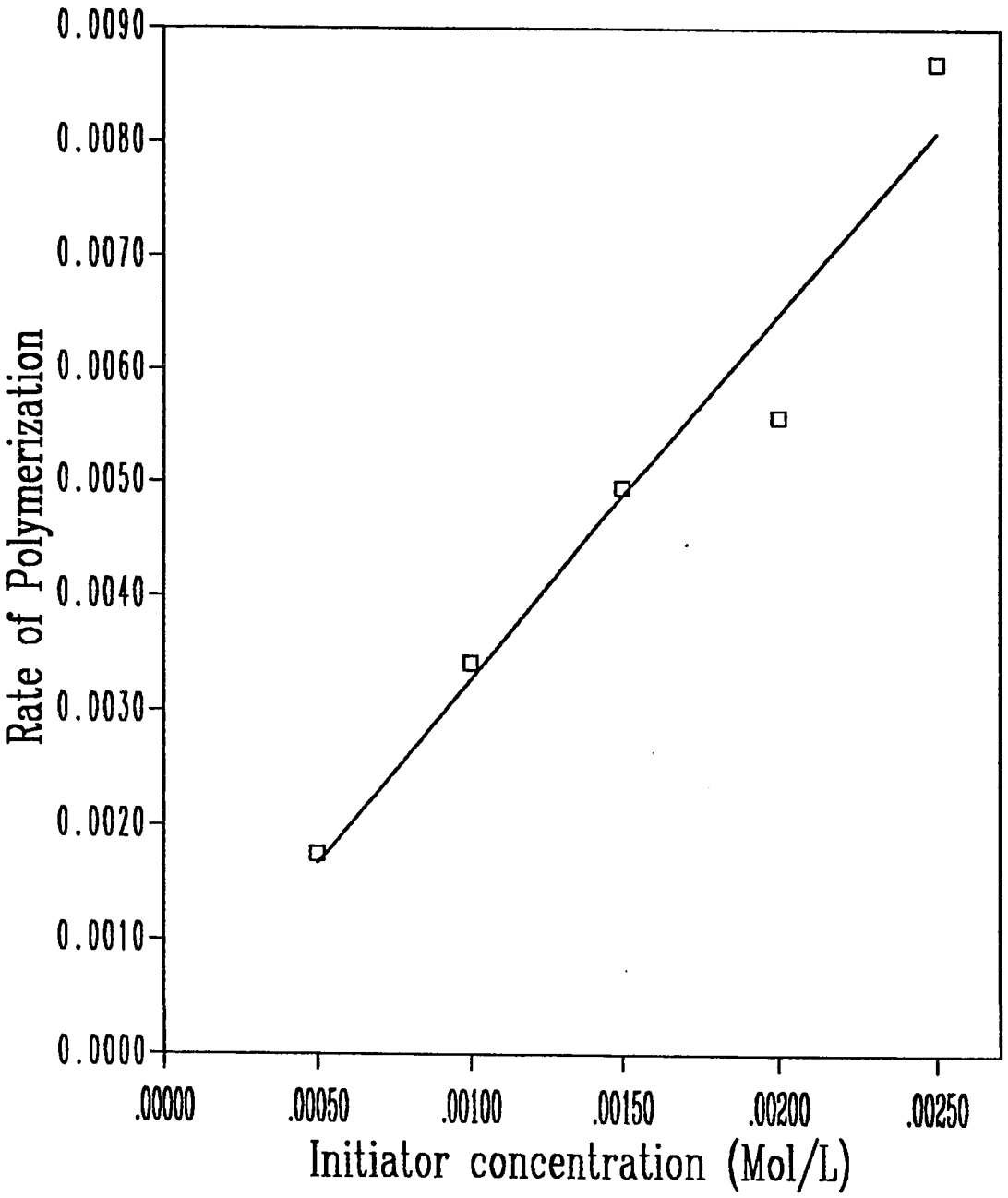


Figure 3.9 : Photopolymerization of cyclohexene oxide by using different concentration of salt **2** after 20 min irradiation. (CHO-1b)

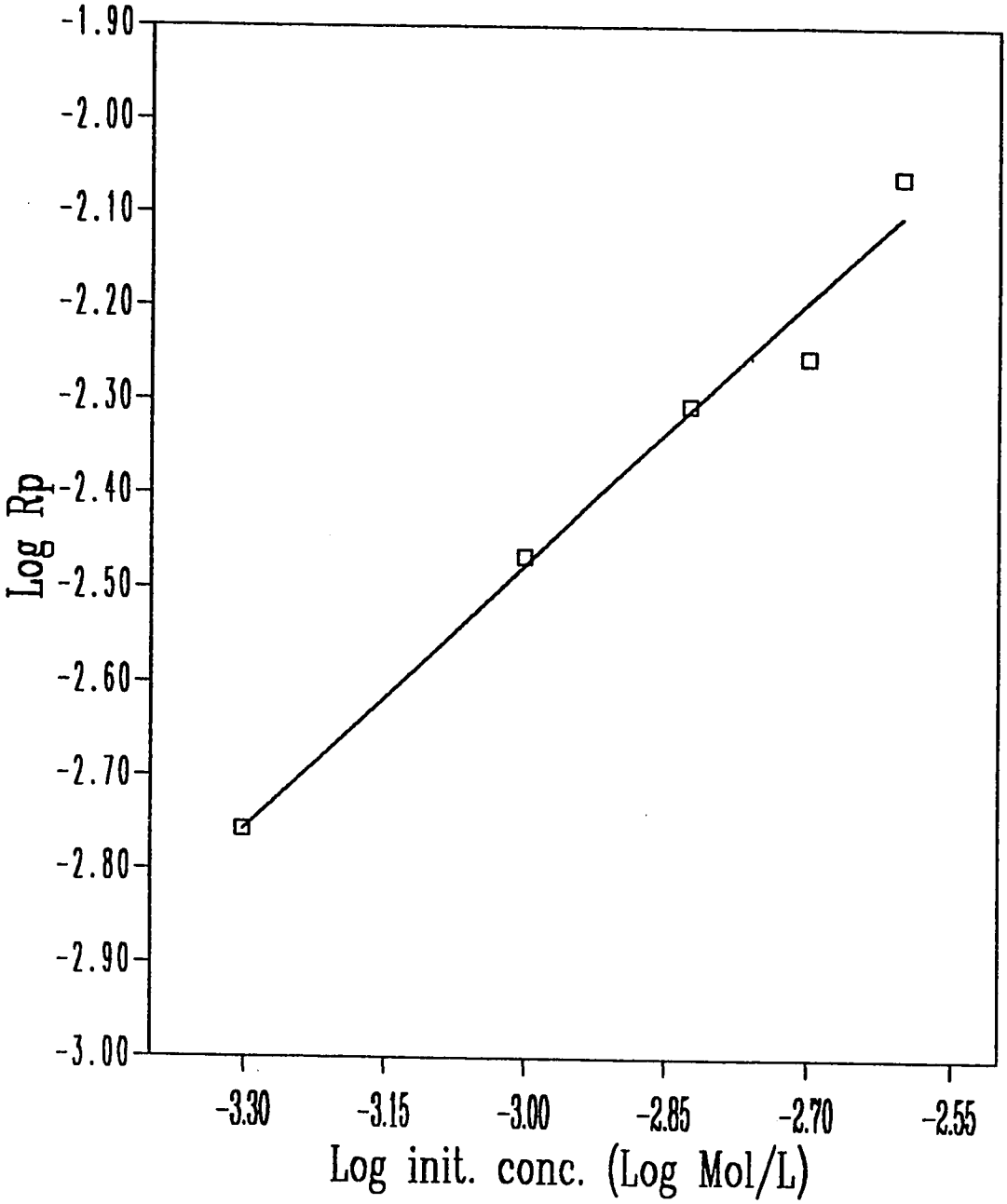


Figure 3.10 : Photopolymerization of cyclohexene oxide by using different concentration of salt **2** after 20 min irradiation. (CHO-1c)

Figure (3.11) shows photopolymerization initiated by methacyltriphenyl phosphonium salt **9**. It is clear that polymerization proceeds without an induction period and the conversion to polymer increase with irradiation time. Comparing salt **9** and salt **2**, results indicate that salt **9** gives 35% conversion after 3 hours while salt **2** needs 12 minutes to give that amount of polymer. Accordingly we can assume that salt **2** is more efficient compared to salt **9** by a factor of 15 times.

The U. V. absorption spectrum of salt **9** and its isolated ylid are shown in figure (3.12). The results reported herein clearly indicate that replacement of methyl group by phenyl group led to an increase in the pKa of salt **9**. This increase in acidity in salt **2** has been attributed to withdrawal effect of the phenyl group (relative to alkyl) which decrease the electron density on the hetero atom group. The replacement of phenyl group by bromophenyl group (salt **5**), also might led to a decrease in the pKa of the phosphonium salts. This implies that bromophenyl group is electron withdrawing (or less electron donating) with respect to methyl.

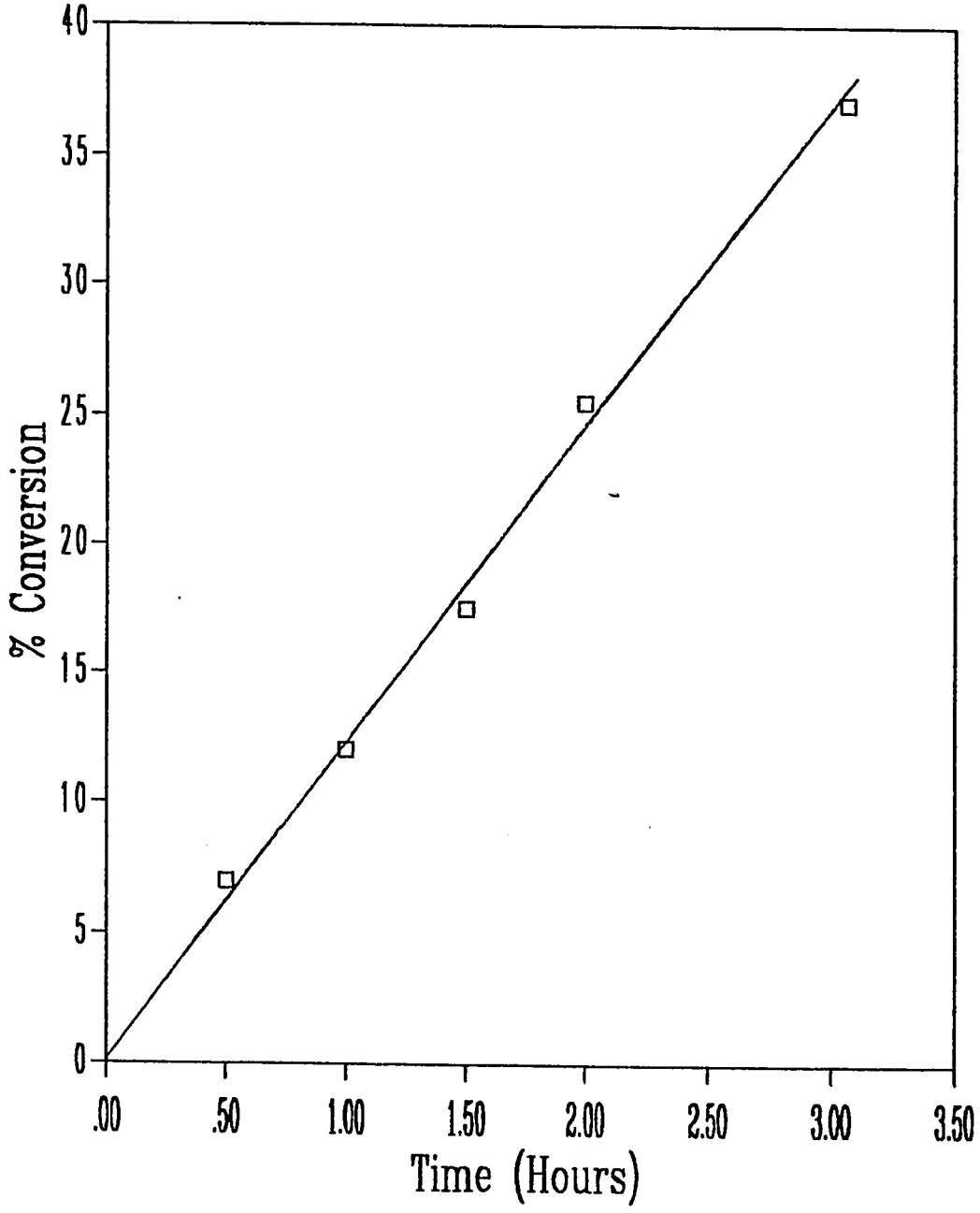


Figure 3.11 : Photopolymerization of cyclohexene oxide by initiator **9.** (CHO-11)

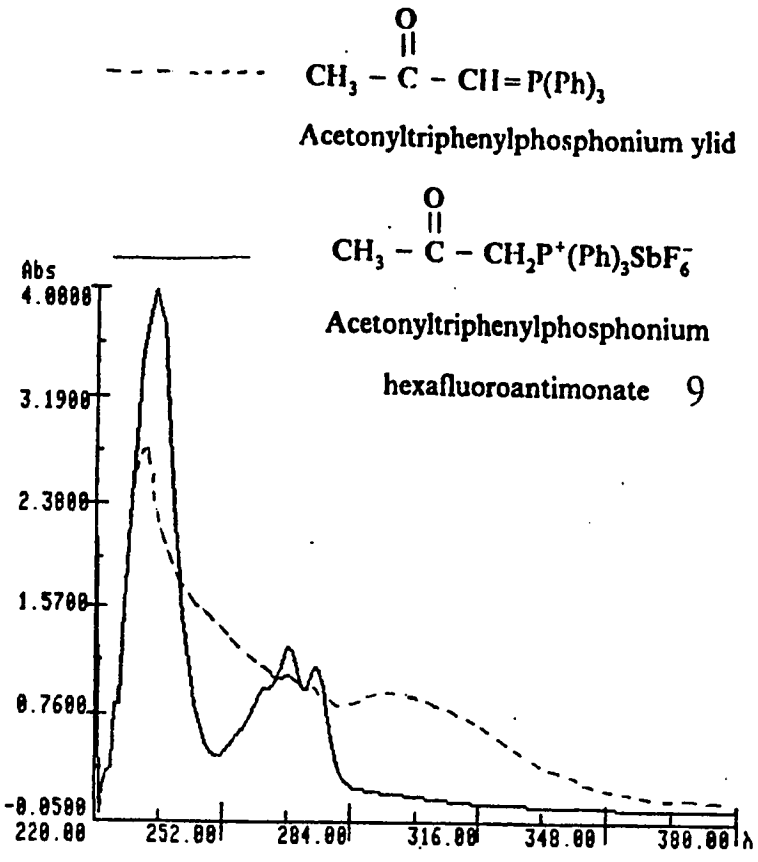
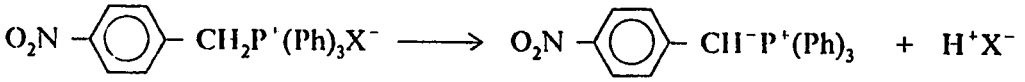
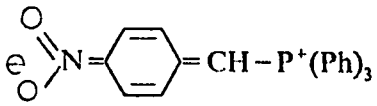


Figure 3.12 : U. V. absorption spectra of salt 9 and ylid 25

Salt **17** did not initiate the polymerization reaction under the reported experimental conditions when the reaction mixture was irradiated for 6 h. It is expected that ylid produce irradiation is very reactive and might decompose to other products before attacking the epoxide as shown in scheme (3.5)





Scheme (3.5)

Photopolymerization with salt **12** and **14** give less conversion to polymer products compared to other salts, however salt **12** is more reactive than salt **14** as shown in table (3.6). The U. V, absorption spectrum of these salts is shown in figure (3.13 and 3.14). Both salts **12** and **14** are expected to be more efficient due to their extended absorption. However, the behavior of the conversion with irradiation time in this system differs from what was expected, which may be due to the fact that both the ylid and the corresponding initiator salt compete for the same light.

Table (3.6) **: Photopolymerization of cyclohexeneoxide**

Initiator	Irradiation time (Minutes)	% Conversion
12	20	7.0
12	40	9.3
14	20	6.1

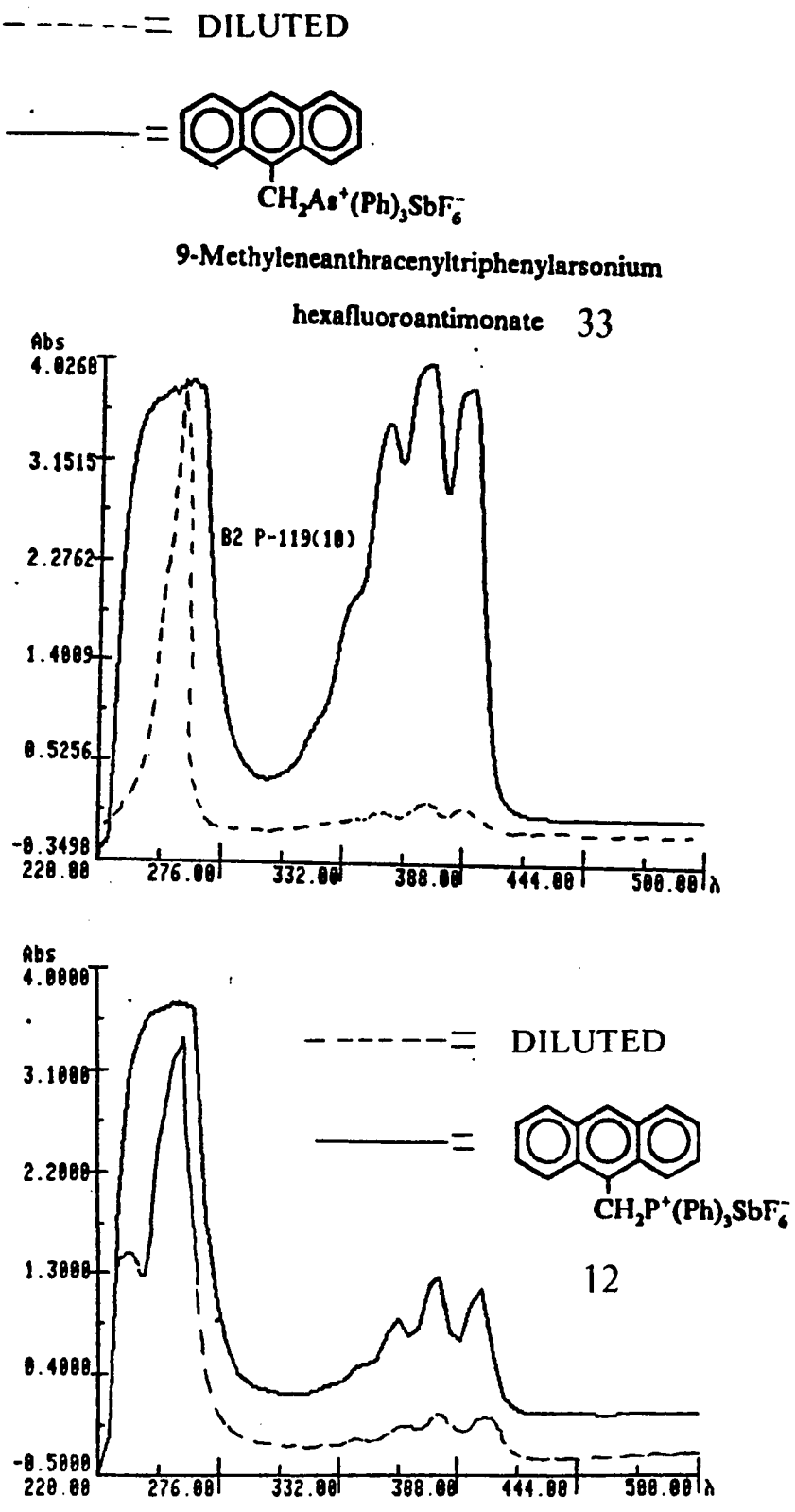
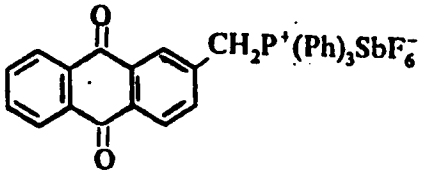
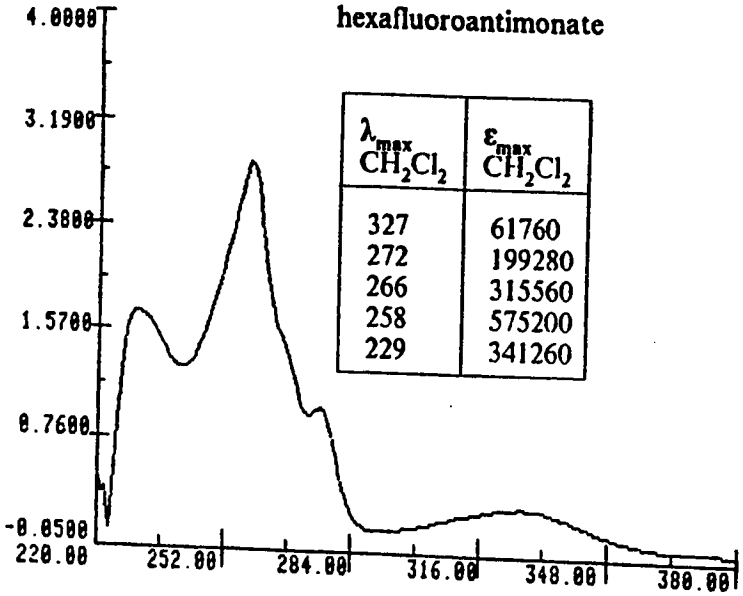


Figure 3.13 : U. V. absorption spectra of salt 12 and 33



2-Methyleneanthraquinonyltriphenylphosphonium hexafluoroantimonate



λ_{max} CH_2Cl_2	ε_{max} CH_2Cl_2
327	61760
272	199280
266	315560
258	575200
229	341260

Figure 3.14 : U. V. absorption spectra of salt 14.

3.5.2 Photopolymerization of cyclohexeneoxide by arsonium salts:-

Figure (3.15) shows that photopolymerization of cyclohexeneoxide proceeds with an induction period that depends on the presence of oxygen in the mixture. When the reaction mixture is degassed, an induction period of about 5 minutes is observed, while without degassing, polymerization started after 13 minutes very fast. These results indicate that a phosphonium group is more effective than an arsonium group in providing stabilization for an adjacent carbanion of the resulting ylids via d-orbital overlap. The stabilization, probably, is via $P_{\pi}-d_{\pi}$ overlap between the carbanion and the onium group if the latter has available empty, low energy d orbital.[82] The effect of concentration of salt **27** in the range $3.0X10^{-3}$ to $6X10^{-3}M$ is shown in figure (3.16). The exponent value of the initiator, determined for the slope of log Rp vs the log concentration of salt [figure (3.17)] is found to be 4.5. Figure (3.18) shows a comparision between the photoinitiation efficiency of salts **2, 9** and **27** on the polymerization rate. This shows that with these photoinitiators the polymerization rate in the first 13 minutes fall in the following sequence

salt (2) > salt (27) > salt (9).

After that time period the sequence could be changed to

salt (27) > salt (2) > salt (9).

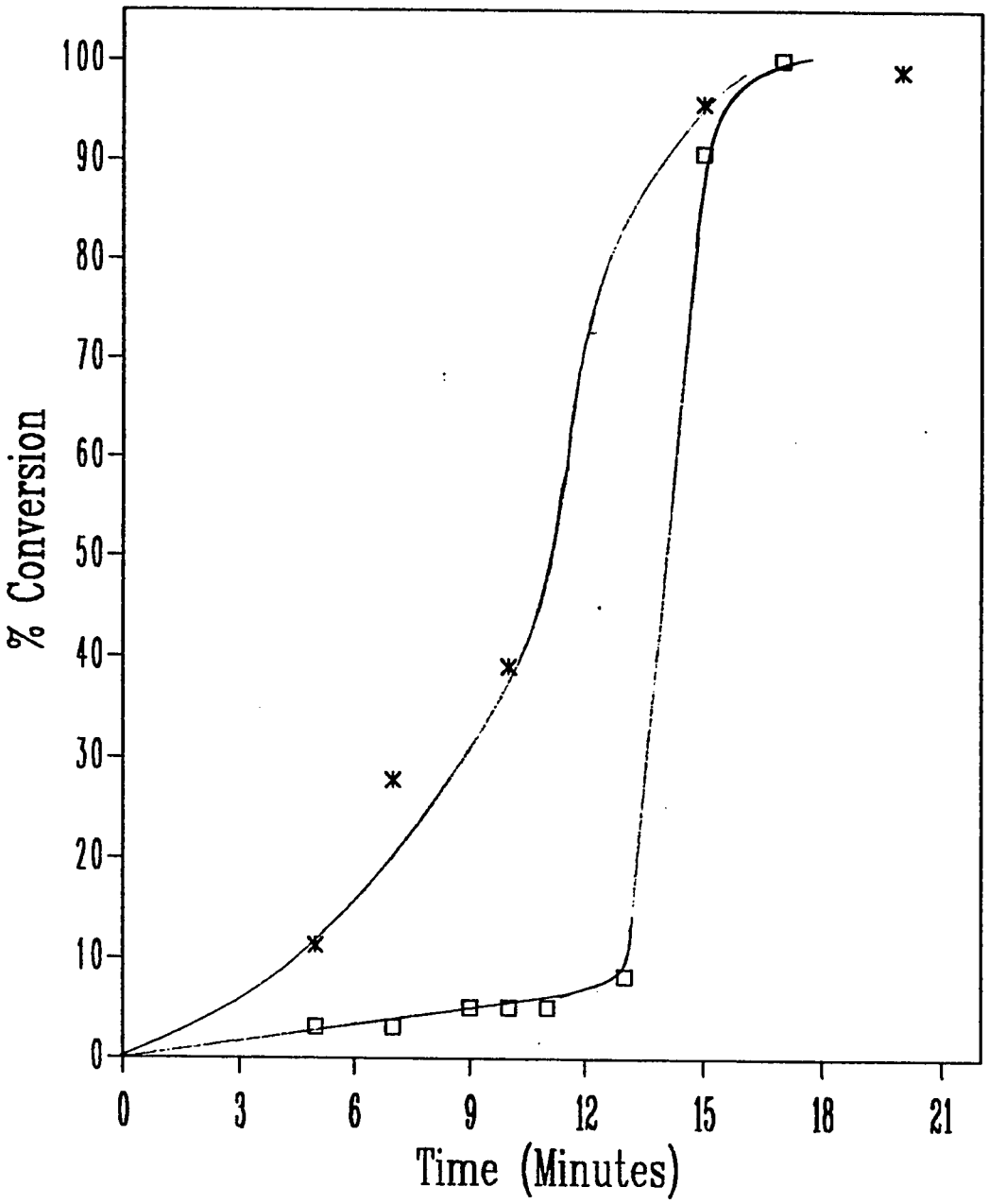


Figure 3.15 : Photopolymerization of cyclohexene oxide by initiator **27**

(✱) degassed, (□) not degassed. (CHO-9,10)

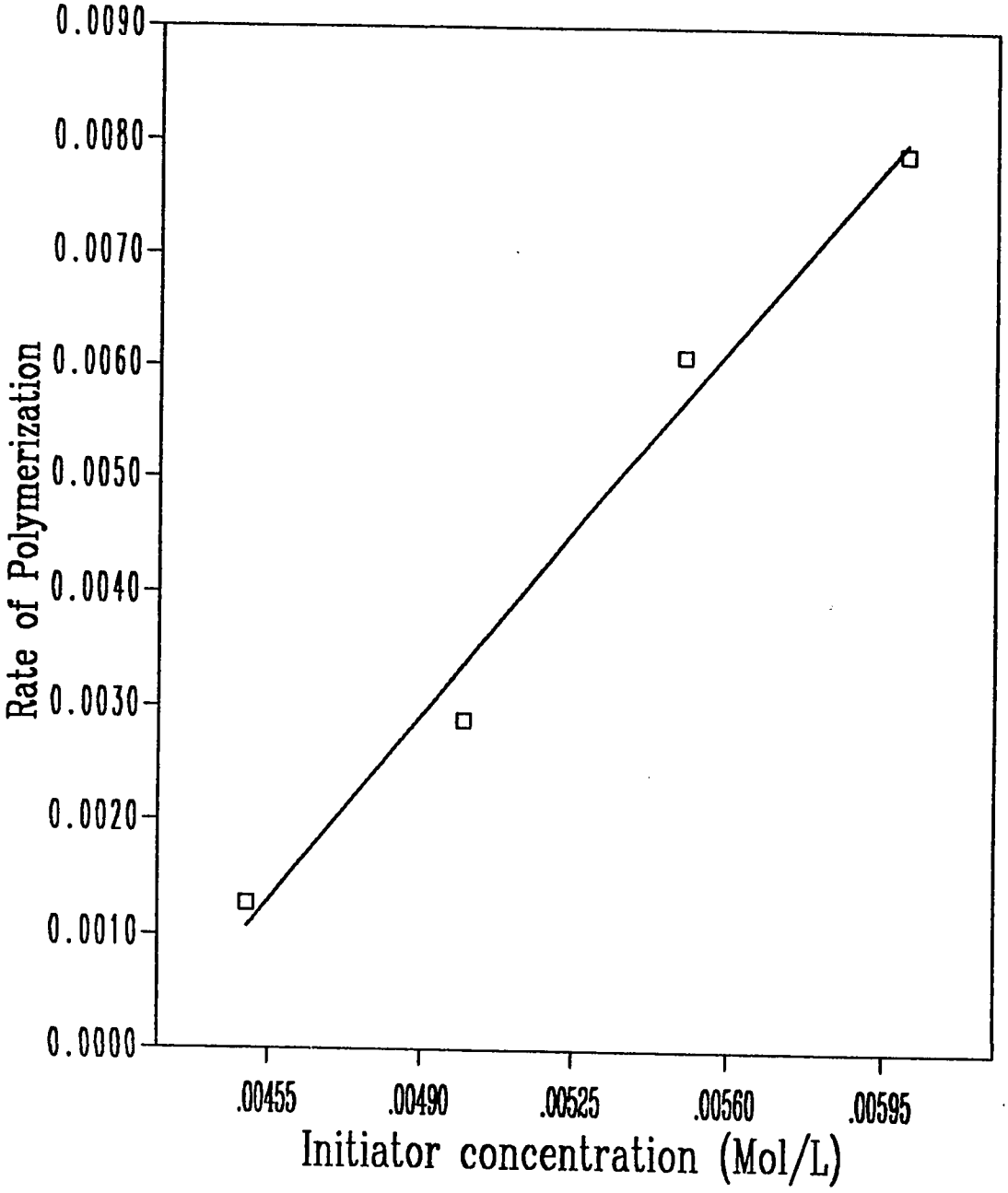


Figure 3.16 : Photopolymerization of cyclohexene oxide by using different concentration of salt **27** after 20 min irradiation. (CHO-8b)

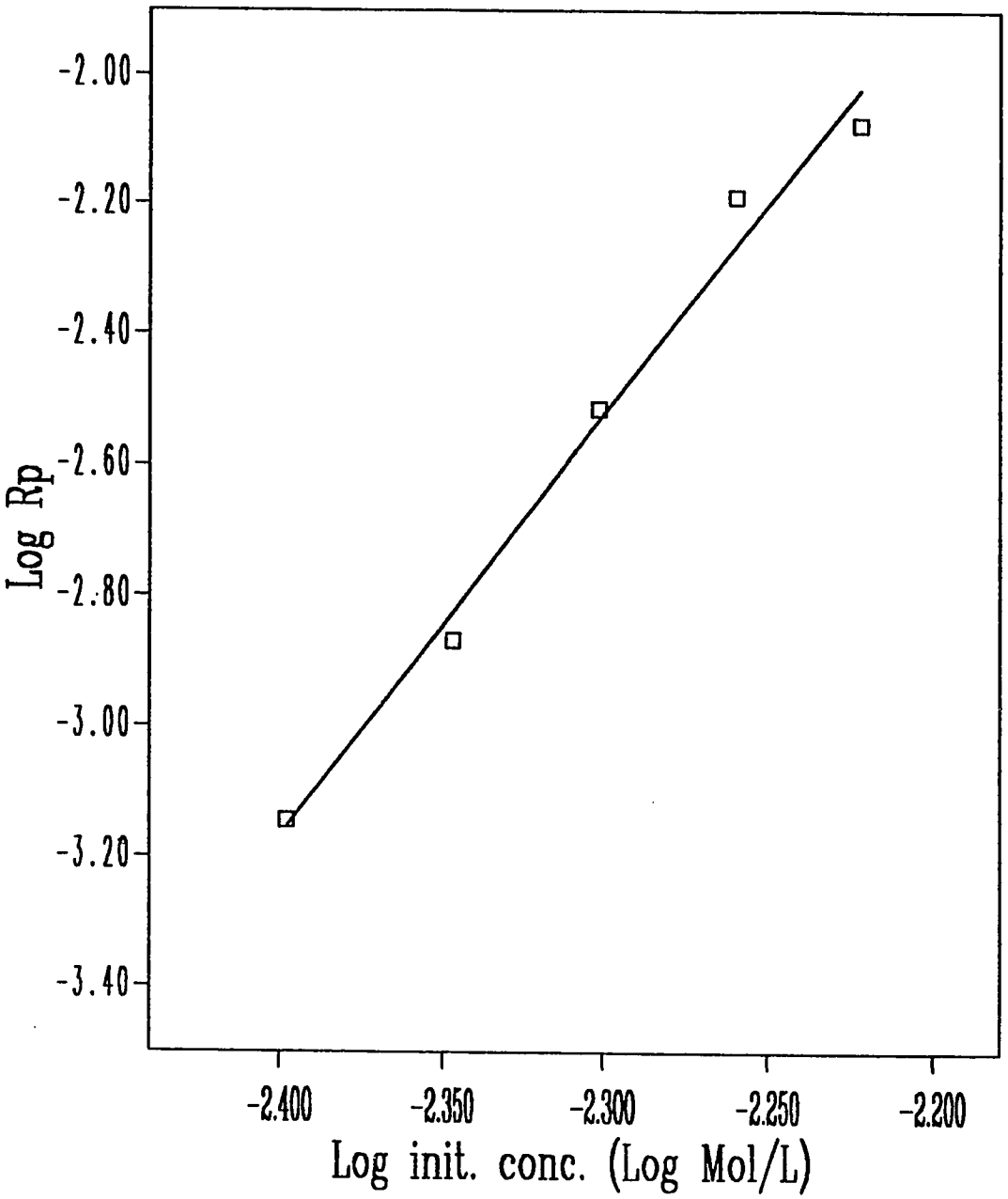


Figure 3.17 : Photopolymerization of cyclohexene oxide by using different concentration of salt **27** after 20 min irradiation. (CHO-8c)

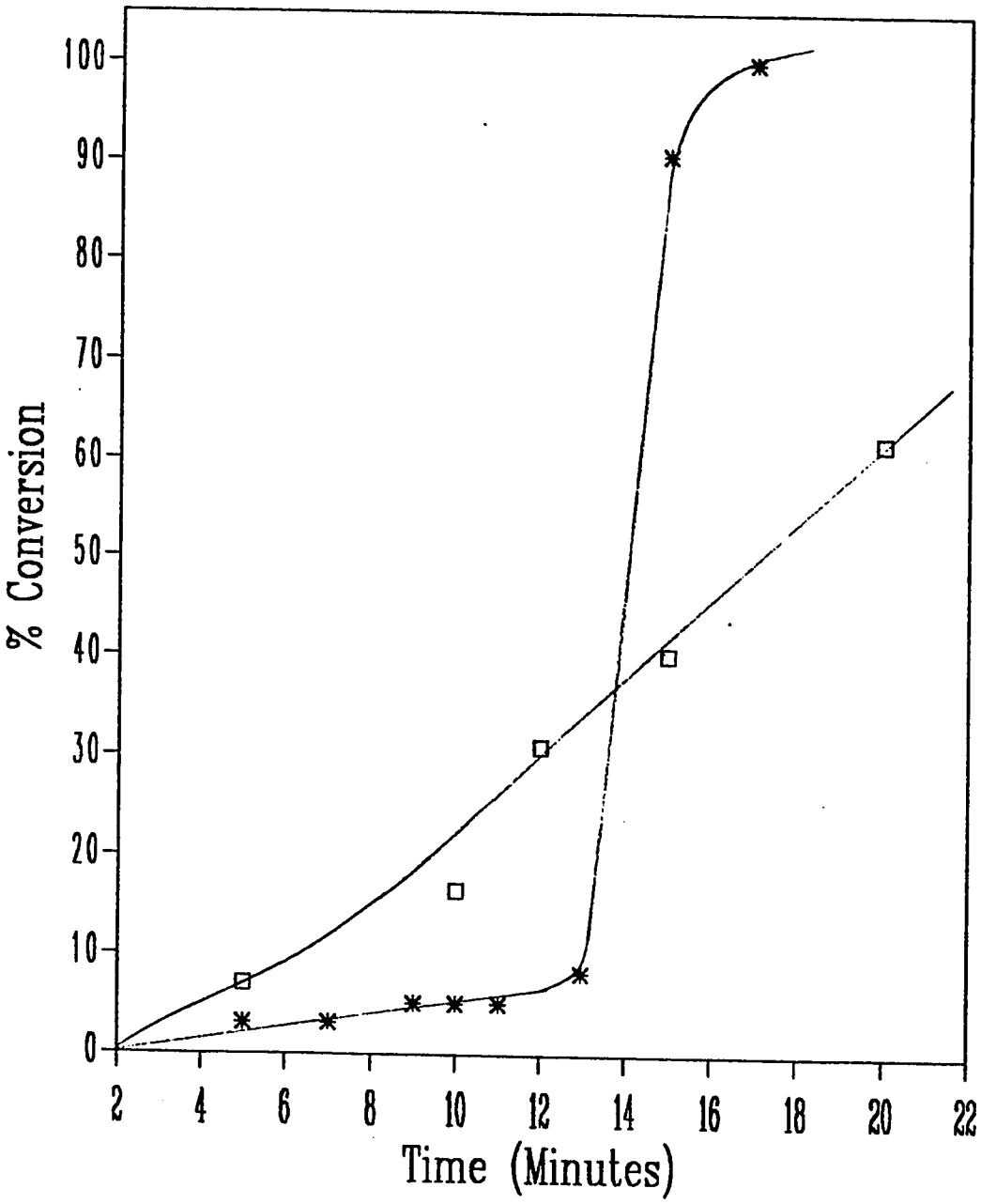


Figure 3.18 : Photopolymerization of cyclohexene oxide by (□) initiator **2**, (✱) initiator **27**. (CHO-5,9,11)

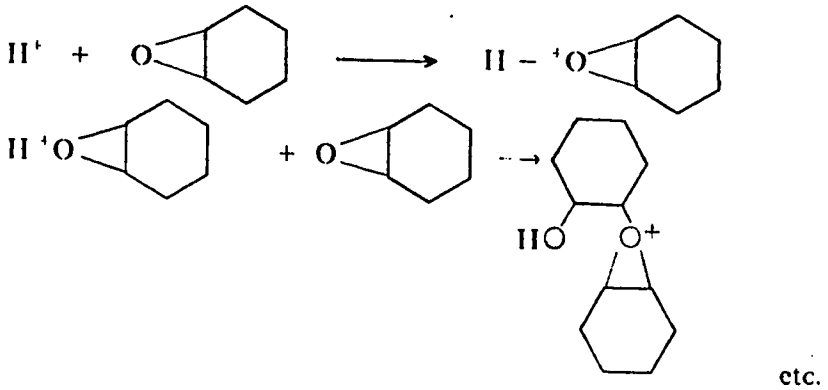
Figure 3.19 shows the difference between the absorption spectra of salt **27** and its isolated ylid **37**. It is clear that ylid has maximum absorption at 328, 234 nm whereas salt absorbed at 256 nm and 229 nm. This shift in the ylid absorption may be used to study quantitatively the salt conversion to ylid by U. V. technique. In a separate experiment we found that isolated ylid **37** dose not initiate the polymerization of cyclohexeneoxide thermally or photochemically. Hence polymerization may be considered to be the results of H^+ initiation, however ylid addition to a reaction mixture inhibit the rate of polymerization due to its competing with the monomer in its reaction with the H^+.

3.5.3 Mechanism of photopolymerization :

According to the reported results a mechanism for initiation of cyclohexene oxide photopolymerization by phenacylphosphonium and arsonium salts can be written as in the following equation :

$$Ph-\overset{O}{\overset{\|}{C}}-CH_2P^+(Ph)_3X^- \xrightarrow{h\nu} Ph-\overset{O}{\overset{\|}{C}}-CH=P(Ph)_3 + H^+X^- \qquad (3.1)$$

The H^+ produced in the photolysis of the salt attacks the more reactive epoxide monomer to generate propagating cyclic onium cation as shown below :

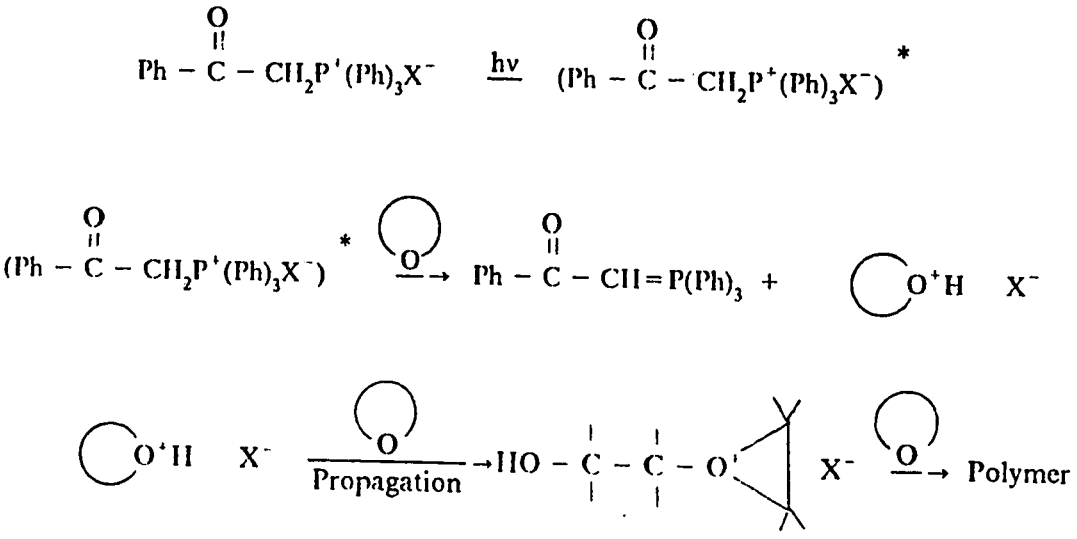


etc.

Scheme (3.6)

The resulting ylid may compete with the epoxide in reacting with the H^+ and terminate the polymerization progerss. This mechanism involves the photoexcitation of the phosphonium salt which rapidly dissociate to form the resonance stabilized ylid, and the protonic acid. Recombination of these two products by a thermal process results in the establishment of steady state concentration of ylid and protonic acid. Solvent or monomer may play an important role in this process by assisting in the removal of a proton from the excited phosphonium salt.

Another mechanism we suggested for initiation of the polymerization of cyclohexeneoxide by these salts consistent with work reported here on pre irradiation of salt followed by addition of monomer in the dark produces extremely vigorous polymerization. This might suggest that the reactive excited state is not simply dissociated into ylid and Bronted acid as shown in equation (3.1) instead of that we expected the following initiation mechanism.



Scheme (3.7)

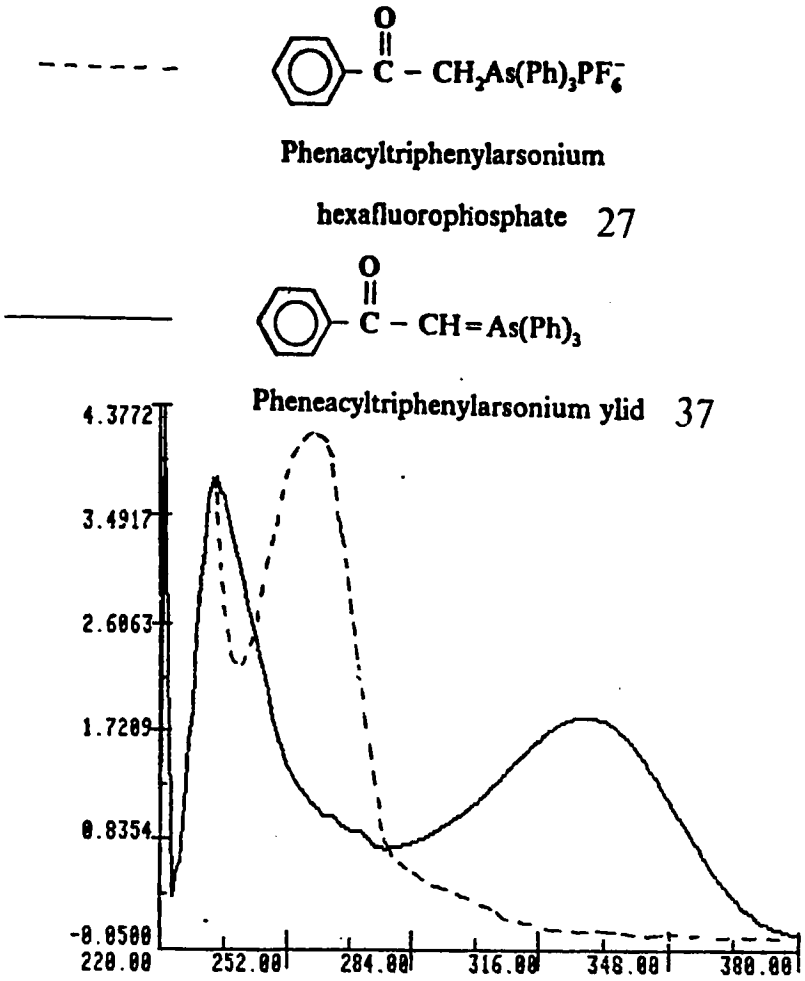


Figure 3.19 : U. V. absorption spectra of salt 27 and ylid 37.

3.5.4. Thermally initiated polymerization :-

It is remarkable that while these salts initiate cationic polymerization when the reaction mixture irradiated, in absence of light they display no initiation activity at room temperature (25 °C). In fact salt **2** may be left at 25 °C in the presence of cyclohexene oxide monomer without inducing polymerization for three days. Cyclohexeneoxide was polymerized thermally by phosphonium and arsonium salts. The effect of temperature change on the rate of polymerization was studied. The results are shown graphically in figure (3.20). Polymerization at 50 °C proceeds to give about 7 % conversion after 9 hours without much increase in the conversion after that period, whereas at 70 °C polymerization increases with time to give about 12 % conversion to polymer. This shows increase the temperature from 50 °C to 70 °C almost doubled the amount of polymer produced. A comparision between thermal and photopolymerization using salt **9** is shown in figure (3.21). This shows that at 50 °C very small amount of polymer was produced while much more polymer was recovered at 70 °C. However irradiation of the reaction mixture was the most efficient method of polymerization. Figure (3.22) shows thermal polymerization of cyclohexeneoxide using salt **2** and **27** at 70 °C. The conversion to polymer is higher in case of using salt **2**. This shows that salt **2** is more reactive thermally with cyclohexene oxide monomer to produce the initiating species $H.^{+}$

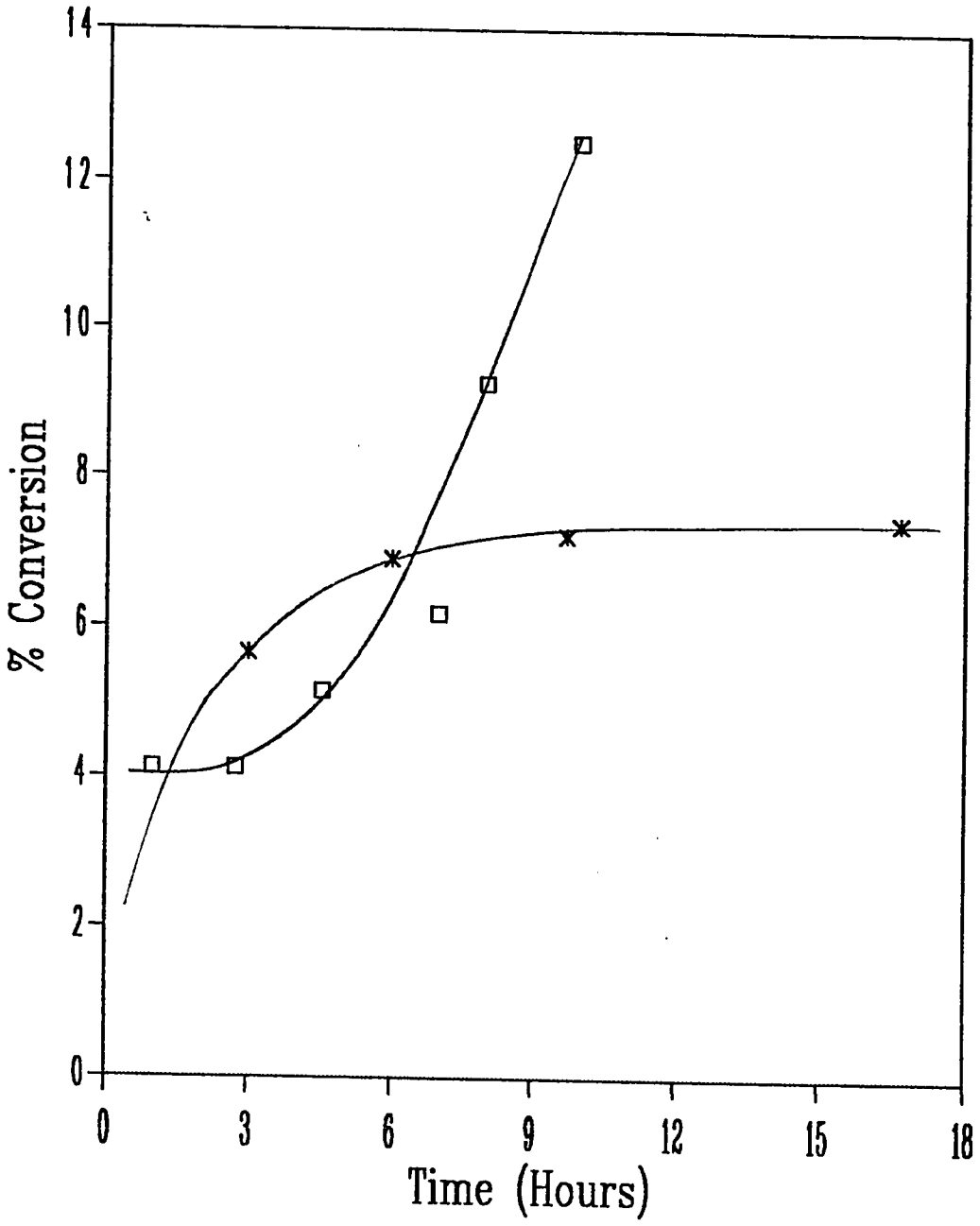


Figure 3.20 : Thermal polymerization of cyclohexene oxide by initiator **2** (□) at 70 °C, (✱) at 50 °C. (CHO-12,13)

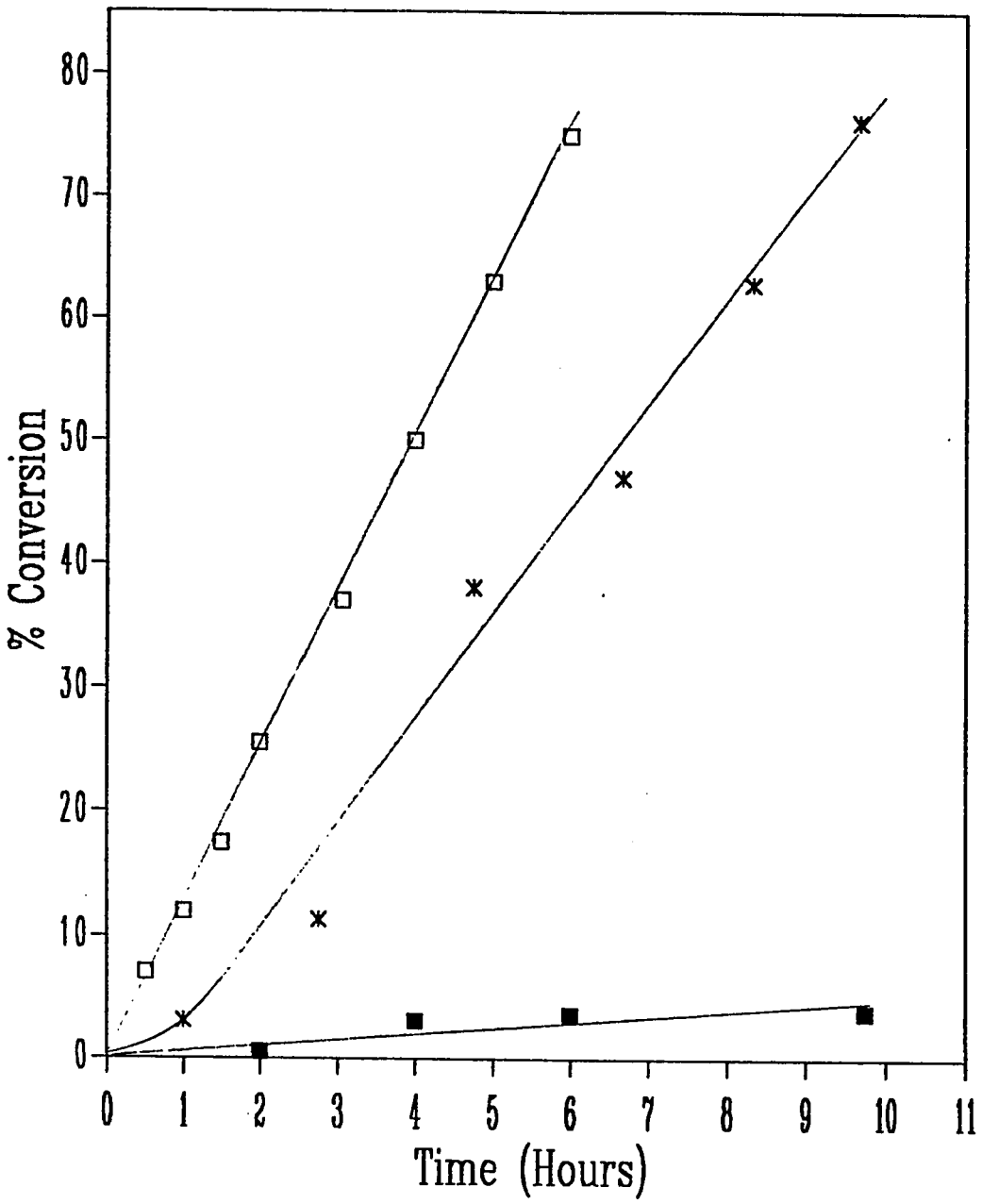


Figure 3.21 : Photo and thermal polymerization of cyclohexene oxide by initiator 9 (□) photo, (✱) thermal at 70 °C, (■) thermal at 50 °C. (CHO-11,16,17)

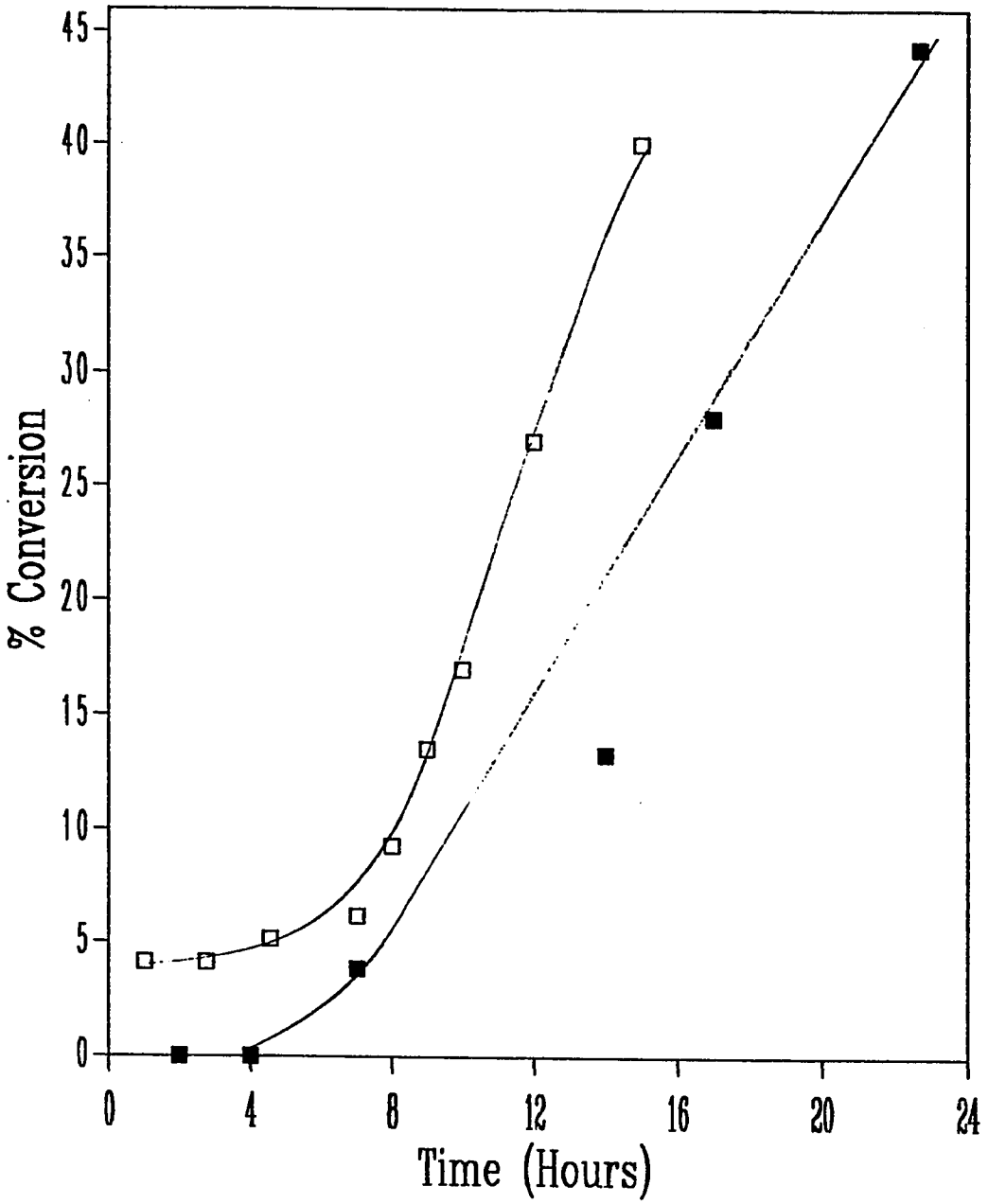
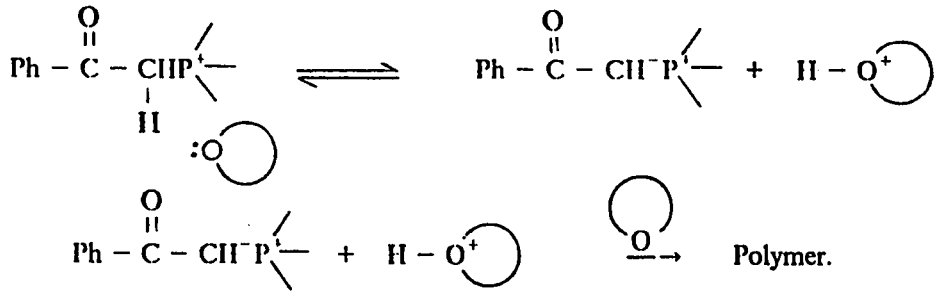


Figure 3.22 : Thermal polymerization of cyclohexene oxide by (□) initiator 2, (■) initiator 27. (CHO-12,14)

3.5.5 Mechanism of thermal polymerization :

We propose the following mechanism for thermal initiation of cyclohexene oxide by phenacylphosphonium and arsonium salts. This mechanism is consistant with work reported by Buddrus et al.[83] On the dehydrohalogination of strongly acidic phosphonium halides by epoxides at 80 °C proceeds as shown in scheme (3.8).



Scheme (3.8)

Here the proton is believed to be abstracted by the oxygen of the epoxide, which give oxonium ion that propagates to a polymer chain

During our work on cyclohexene oxide photopolymerization in presence of phosphonium and arsonium salts, we found that adding triphenyl phosphine or triphenyl arsine has no effect on the rate of polymerization [table (3.7)].

In an attempt to understand the photolysis mechanism of these salts we studied the effect of adding the monomer before and after the irradiation of the salt. Results are reported in table (3.8) and indicate that with salt **27** and **2** irradiation of salt alone for 15 minutes followed by adding cyclohexeneoxide gives about 50 % conversion in case of salt **27** and 11 % in case of salt **2**. This shows that salt **27** is more reactive photochemically than salt **2**, at least in H^+ production.

Table (3.7) : **Photopolymerization of cyclohexeneoxide**

Additive	Irradiation time (Minutes)	% Conversion
Triaryl arsine	65	zero
Triphenyl phosphine	65	zero
Tetrabutylammonium hexafluorophosphate	190	zero
--------	660	zero

Table (3.8) : **Effect of irradiation of salt on the rate of polymerisation of cyclohexeneoxide.**

Initiator No.	Irradiation time of salt alone(Minutes)	Total time after mixing (minutes)	% Conversion
27	60	.05	100
27	15	.50	49.6
2	60	.05	100
2	15	.50	11.3
23	----	60	zero
23 & 2	----	20	zero

3.6 POLYMERIZATION OF P-METHYLSTYRENE :-

p-Methylstyrene is reactive monomer in cationic polymerization photoinitiated by some of the phosphonium and arsonium salts prepared in this work. Figure (3.23) shows the effect of adding salt **2** on the polymerization of p-methylstyrene compared to its polymerization alone, it is clear that salt inhances the rate of polymerization and increase the polymer conversion.

The shape of curve in figure (3.24) indicates that rate of polymerization is also affected by light intensity, at 12 amp. output current (11.24×10^{17} photons/sec. cm^2).

Photosensitization of p-methylstyrene polymerization was carried out using pyrene and N-methylphenothiazine photosensitizers. Figure (3.25) shows that addition of pyrene gives rapid initiation and 100% conversion to polymer was obtained in about 30 minutes, while N-methylphenothiazine seems to inhibit the polymerization reaction as less polymer was obtained compared to salt **27** alone. Addition of more pyrene to the reaction mixture of pyrene and salt **27** in range from 0.025×10^{-3} to 2.5×10^{-3} gives no significant increase in the amount of polymer obtained.

A comparison between salt **2**, **3**, **5**, and **9** (figure 3.26) on the rate of polymerization shows the efficiency of these salts in the photopolymerization of p-methylstyrene fall in the following sequence.

salt 2 > salt 5 > salt 9 > salt 3

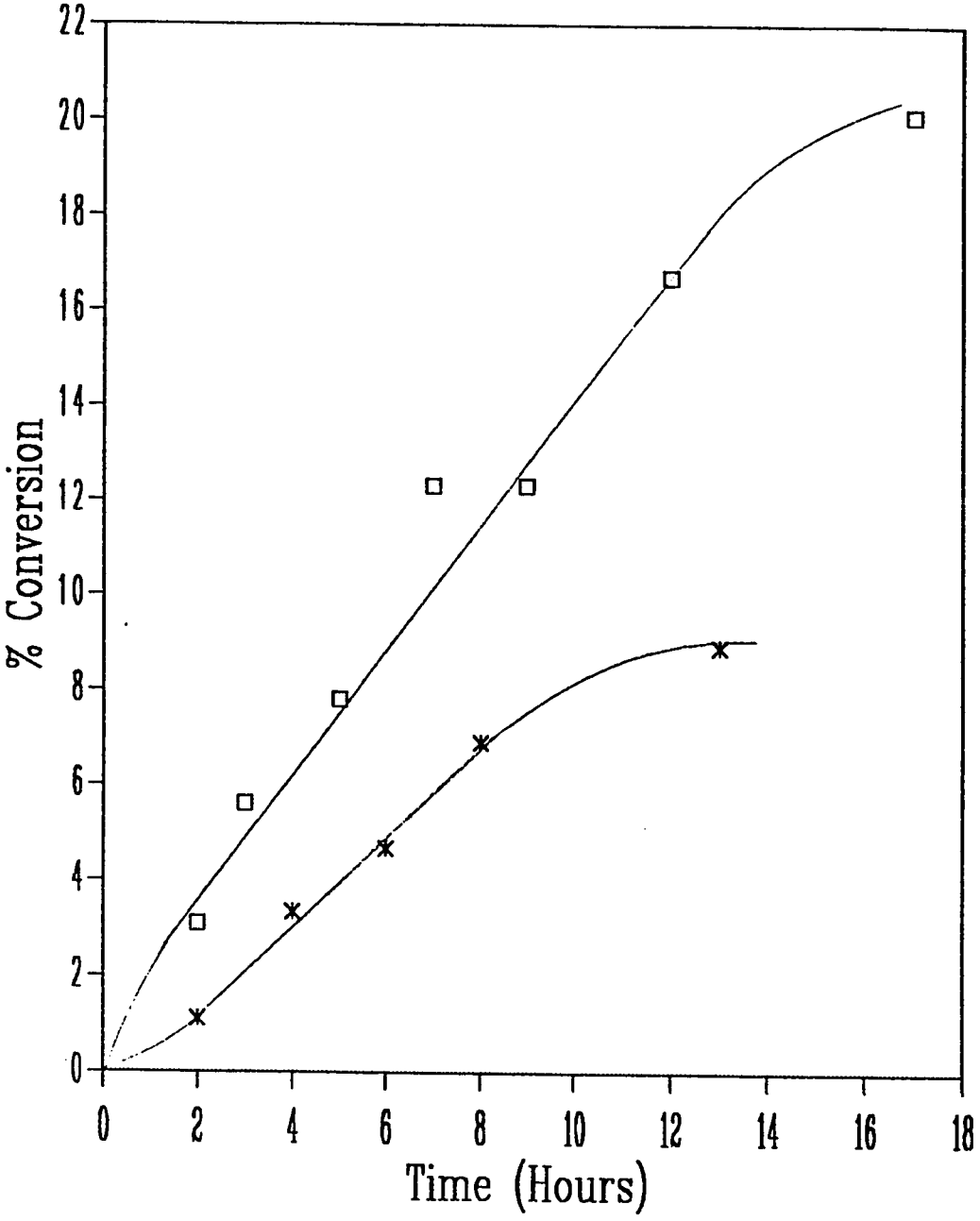


Figure 3.23 : Photopolymerization of p-methylstyrene, (✱) alone, (□) initiator **2** (PMS-1a,1b)

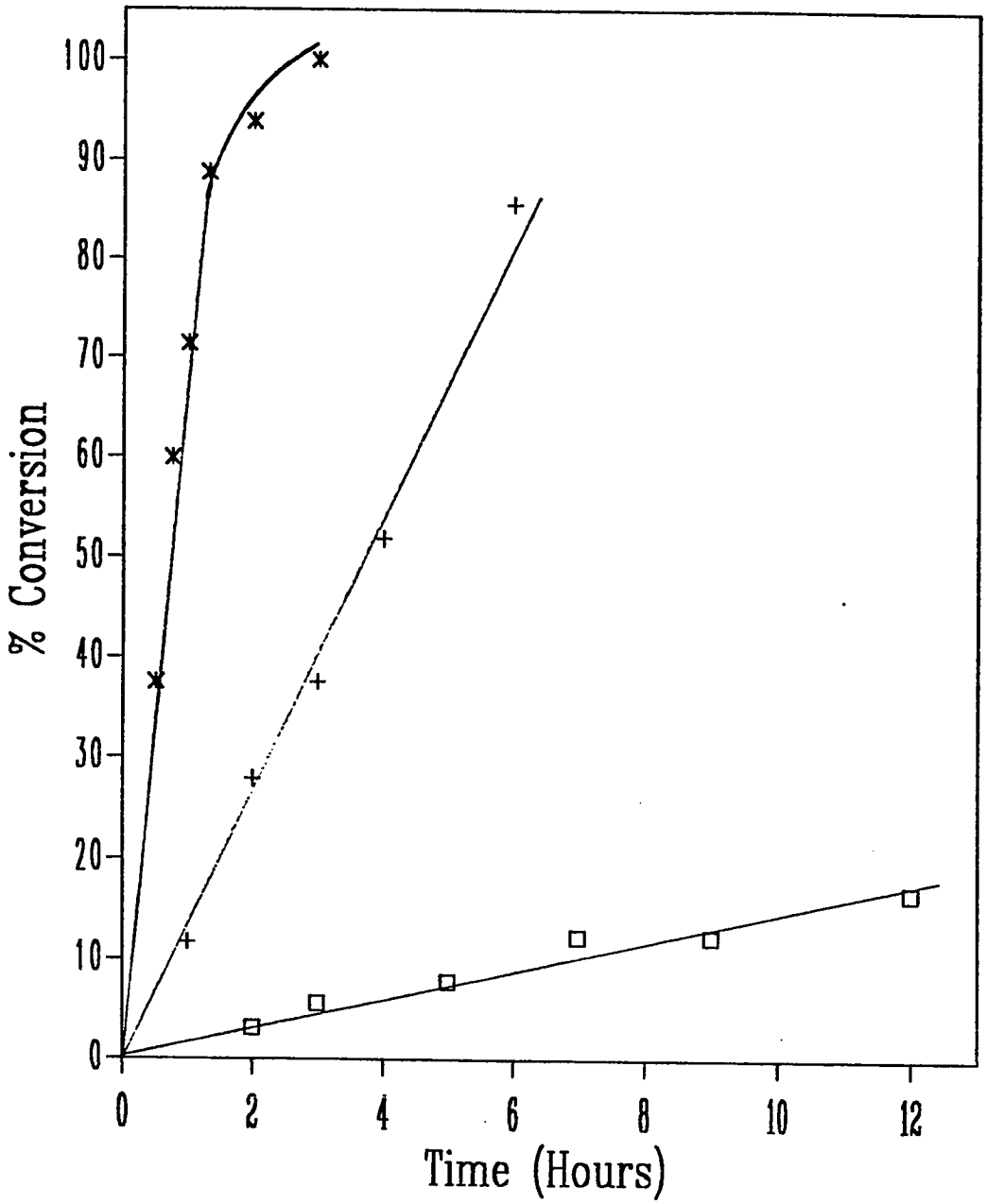


Figure 3.24 : Photopolymerization of p-methylstyrene by (□) initiator **2**, (✱) initiator **27** at 12 amp. output current, (+) initiator **27** at 8 amp. output current, (PMS-1,4,15)

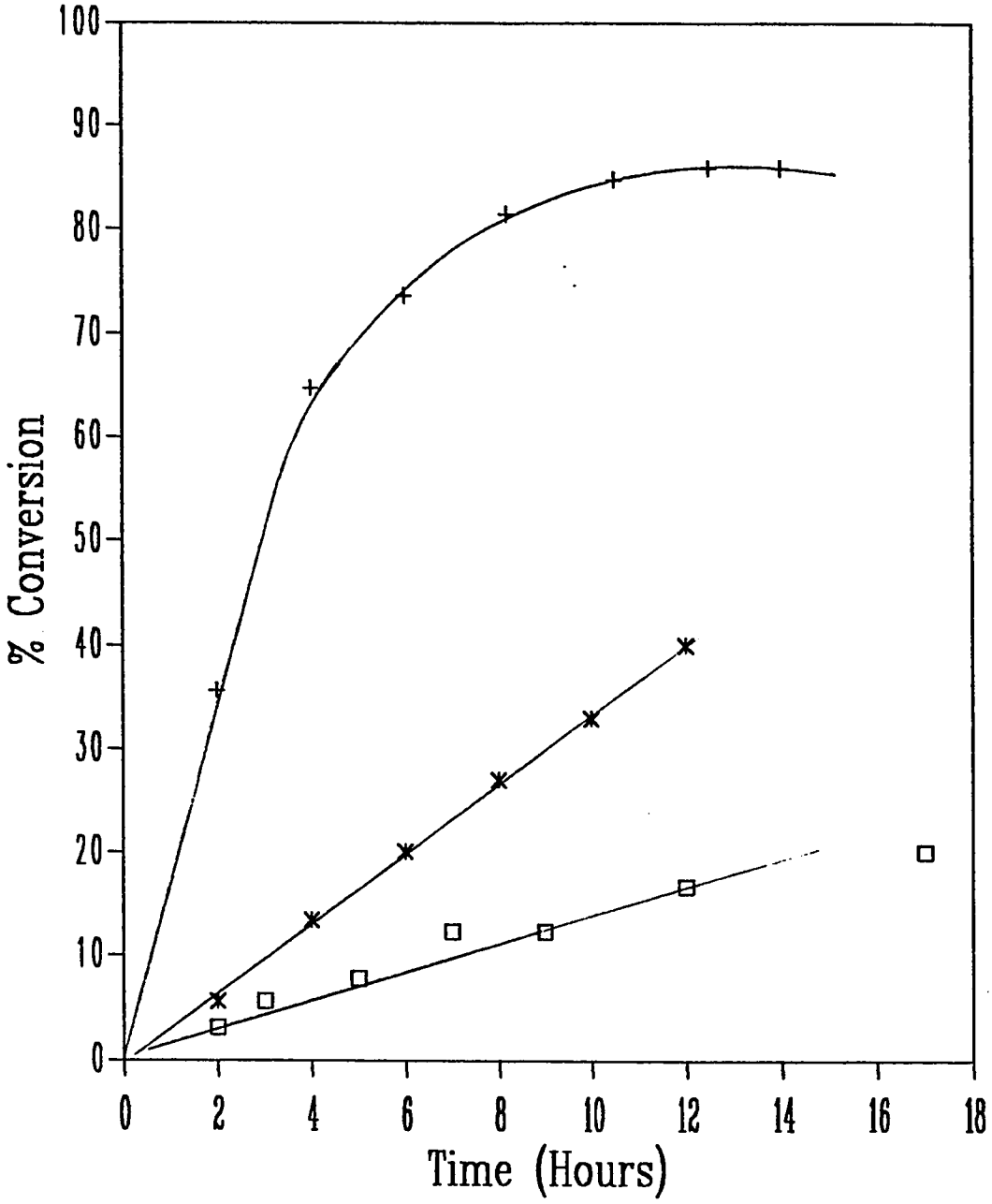


Figure 3.25 : Photopolymerization of p-methylstyrene by (□) initiator **2**, (✱) initiator **2** + N-methylphenothiazine, (+) initiator **2** + pyrene. (PMS-1a,2,3)

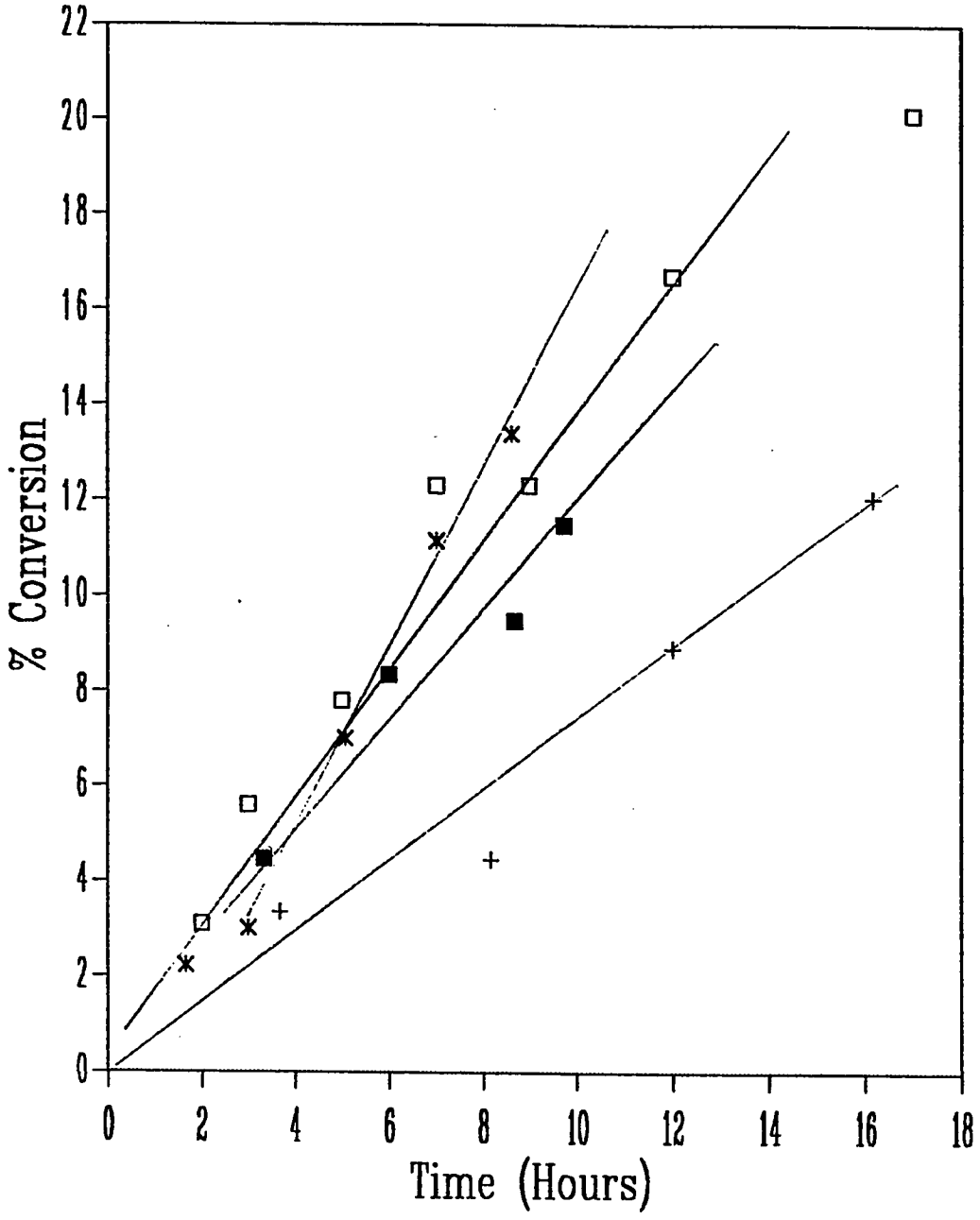


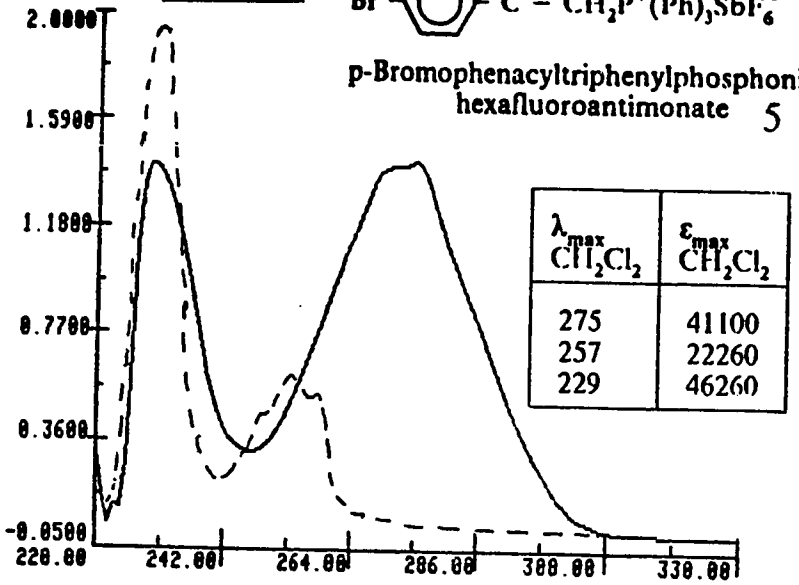
Figure 3.26 : Photopolymerization of p-methylstyrene by (+) initiator 3, (■) initiator 9, (✱) initiator 5, (□) initiator 2. (PMS-1a,8,9,10)

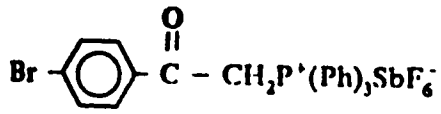
The difference between the behavior of the salt **2** and **3** is due to the anion stability as described before, also salts **5** and **9** differ in structure and absorption spectrum (figure 3.28). Results in figure 3.24 are shown to compare the efficiency of salts **2** and **27**, these results indicate that 5% conversion to polymer was obtained after 3 h with salt **2**, on the other hand salt **27** gives 100% conversion under the same conditions. It is also clear that even at a lower light intensity (8 amp. output current) salt **27** is more active than salt **2**. The same figure also shows as light intensity increases polymer conversion increases.

Figure 3.29 shows the result of polymerization by initiator **17** at different light intensity and initiator **19** under the same condition. These results indicate that salt **17** is more efficient compared to salt **19**. It is also clear that polymerization rate is dependant on light intensity. The interaction of triphenylphosphine and triphenylarsine with p-methylstyrene in dichloromethane was investigated to test the ability of these species on initiation of the polymerization reaction. Data in table (3.9) suggests that these species act as inhibitors in cationic polymerization of p-methylstyrene, since the amount of polymer obtained upon irradiation of monomer alone was twice as much as that in the presence of these species.

Table (3.9) **: Photopolymerization of p-Methylsyrene**

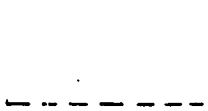
Additive	Irradiation time (Minutes)	% Conversion
Triaryl arsine	480	2.3
Triphenyl phosphine	480	2.3
----------	480	4.68





p-Bromophenacyltriphenylphosphonium hexafluoroantimonate 5

λ_{max} CH_2Cl_2	ε_{max} CH_2Cl_2
275	41100
257	22260
229	46260



Acetonyltriphenylphosphonium hexafluoroantimonate 9

λ_{max} CH_2Cl_2	ε_{max} CH_2Cl_2
275	87000
268	88000
235	84000

Figure 3.28 : U. V. absorption spectra of salt 5. and salt 9.

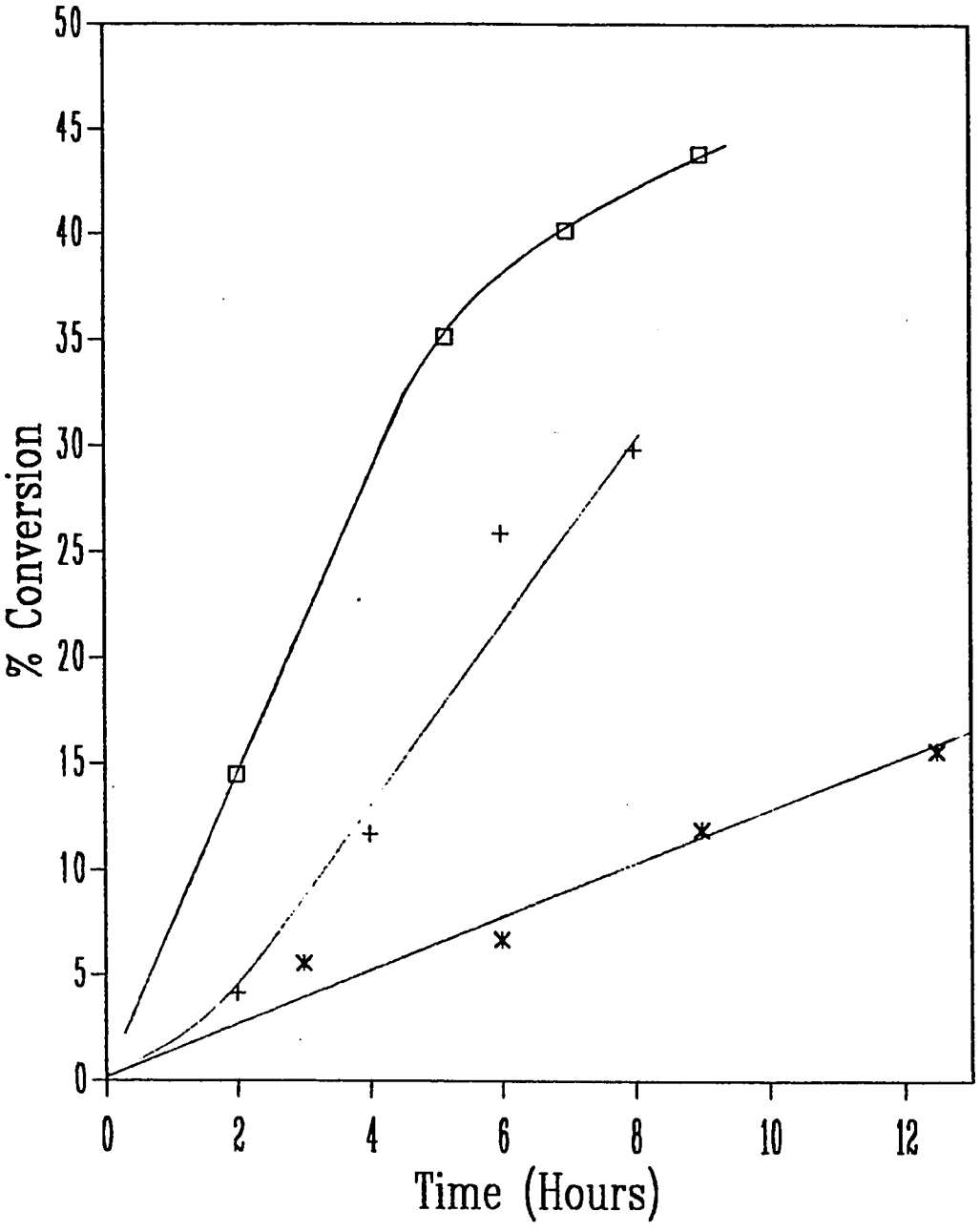


Figure 3.29 : Photopolymerization of p-methylstyrene by (✱) initiator **19**, (□) initiator **17** at 12 amp. current, (+) initiator **17** at 8 amp current. (PMS-11,12,13 = 11213)

The effect of irradiation of salt alone followed by the addition of monomer is shown in table (3.10). Salt **27** irradiation for 20 minutes in dichloromethane followed by the monomer addition gives no polymer when the reaction mixture was left for 10 hours, however, irradiation of salt **2** for 60 minutes followed by the monomer addition under the same conditions gives 90% conversion to polymer. These results suggested that for polymerization with salt **27** interaction between photoexcited monomer with the salt is necessary for initiation.

Table (3.10) **: Effect of irradiation of salt on the rate of polymerisation of p-Methylstyrene.**

Initiator No.	Irradiation time of salt alone(Minutes)	Total time after mixing (minutes)	% Conversion
27	60	180	5.2
27	60	660	6.7
2	60	660	96

3.7 POLYMERIZATION OF STYRENE :-

The results of styrene photopolymerization by salt **2, 9** and the active ylid **23** are presented in figure (3.30). These results show that salt **2** is the only active photoinitiator for styrene polymerization, while salt **9** and ylid **23** are not active cationic photoinitiators for this monomer. In fact some termination is taking place due to the presence of these salts since in the absence of these species styrene polymerization gives more polymer.

Result in figure (3.31) shows the polymerization using salt **17** and **19** and are compared to the efficiency of salt **2.** It is clear that salt **17** is more efficient as photoinitiator compared to salt **2** and salt **19** is less active than both **17** and **2.**

The photosensitization of styrene photopolymerization with salt **27** is shown in figure (3.32). In this study while pyrene is shown to be an excellent sensitizer, N-methylphenothiazine is shown to be an inhibitor under the same experimental conditions. We also observed no significant increase in the rate of polymerization as pyrene concentration was increased from range $0.025x10^{-3}$ to $2.5x10.^{-3}$ These results indicate an interaction between the excited state of the salt and N-methylphenothiazine to produce a stable product which is not capable of initiating the styrene polymerization.

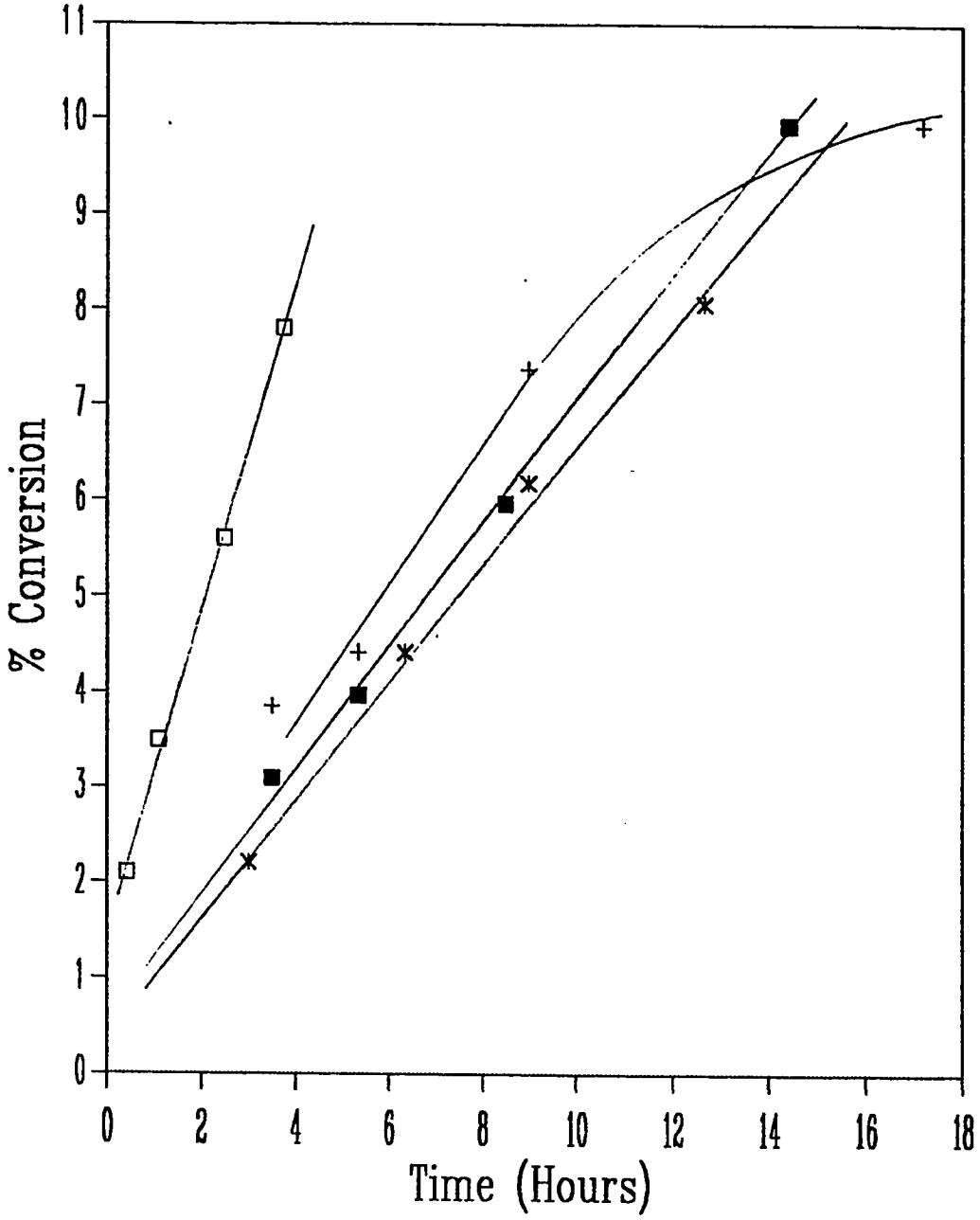


Figure 3.30 : Photopolymerization of styrene, (+) alone, (■) ylid **23**, (✱) initiator **9**, (□) initiator **2**. (STY-1,7,8,9)

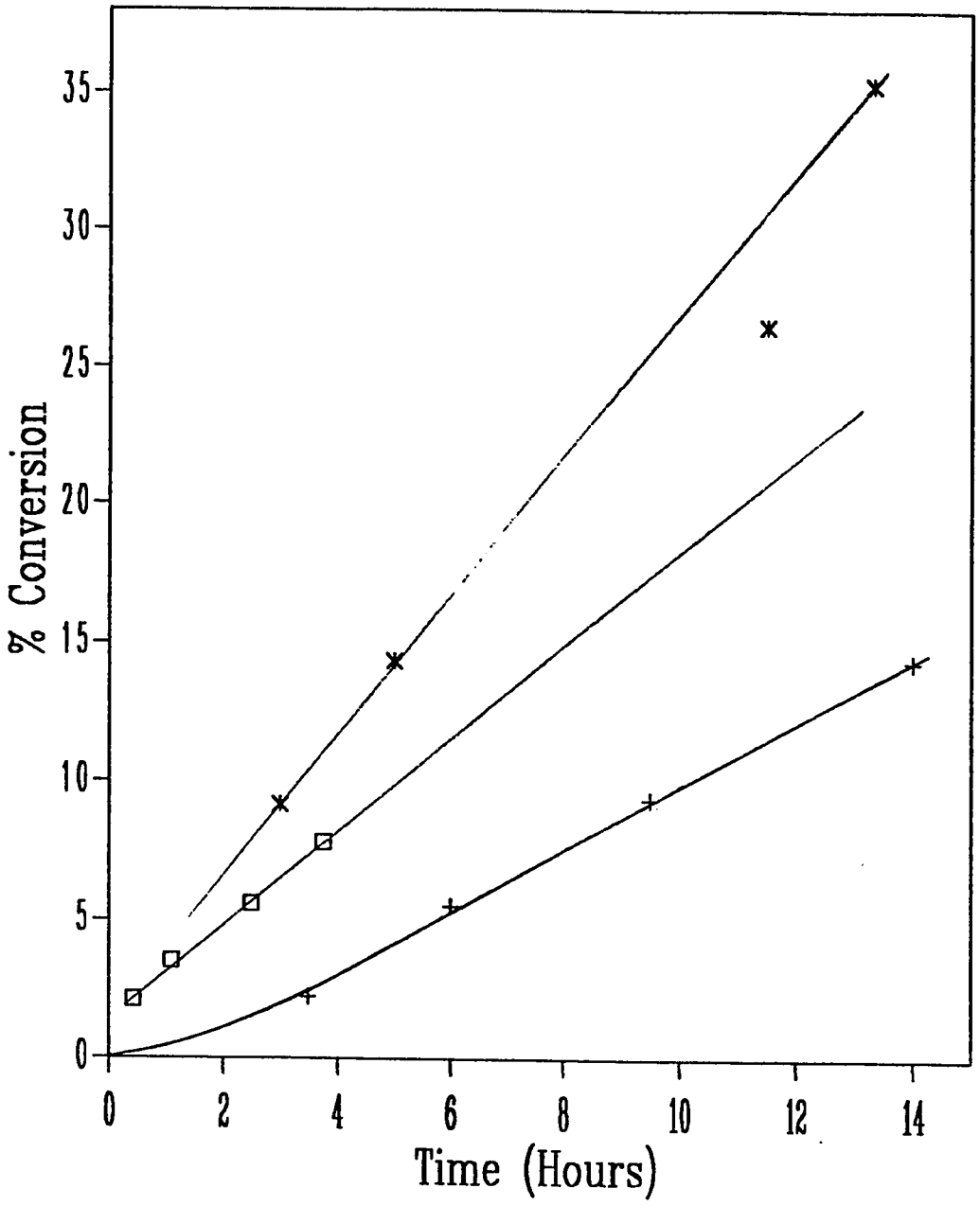


Figure 3.31 : Photopolymerization of styrene by (□) initiator **2**, (✱) initiator **17**, (+) initiator **19**. (STY-1,10,11)

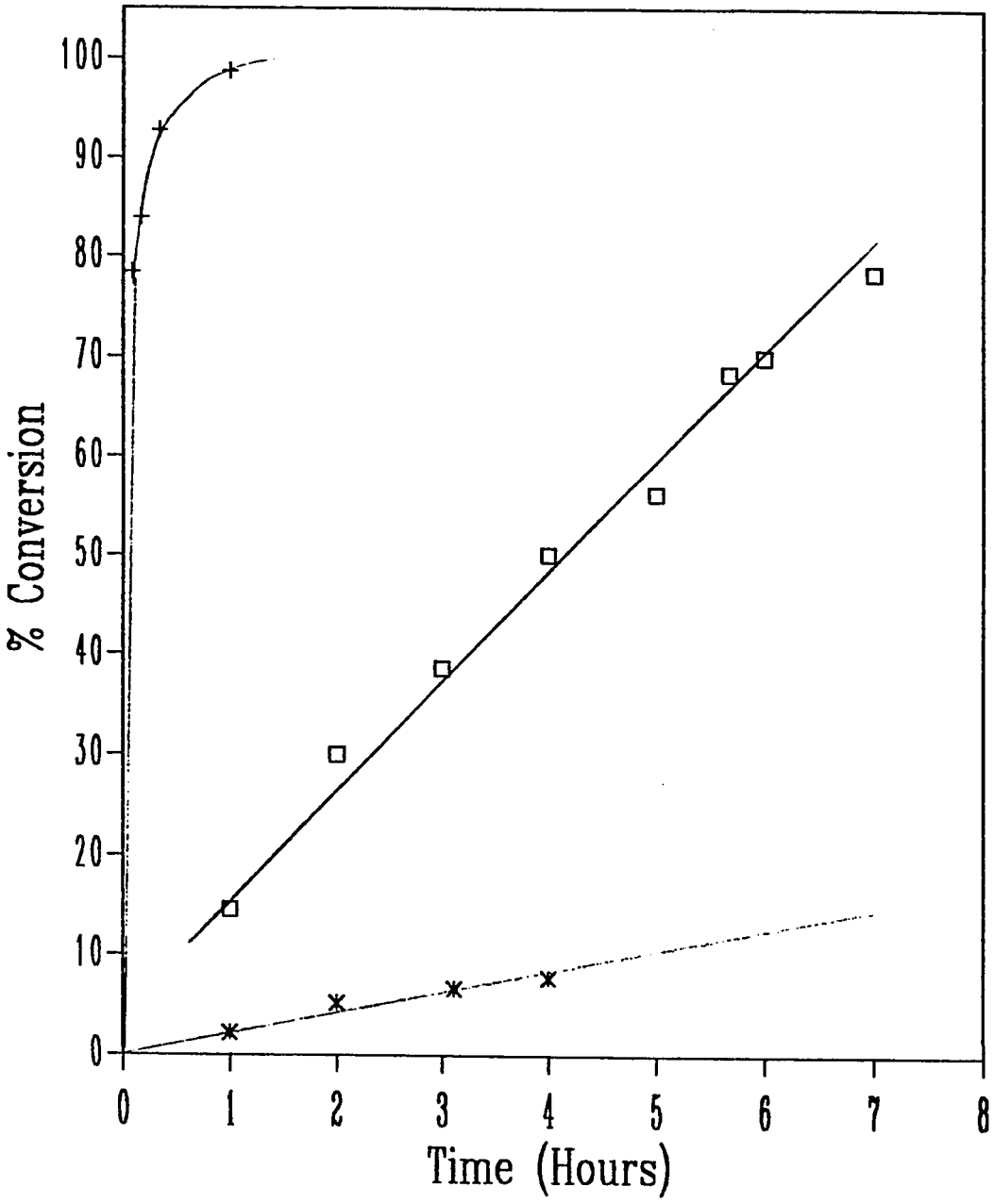


Figure 3.32 : Photopolymerization of styrene by (□) initiator **27**, (✱) initiator **27** + N-methylphenothiazine, (+) initiator **27** + pyrene. (STY-3,4,5)

Table (3.11) shows both triphenylphosphine and triphenylarsine can act equally as inhibitors in the photopolymerization of styrene. These results also show, under the same conditions, the amount of polymer in the presence of any of these species reduced to its half when compared with the photopolymerization of styrene alone.

Table (3.11) **: Photopolymerization of Styrene**

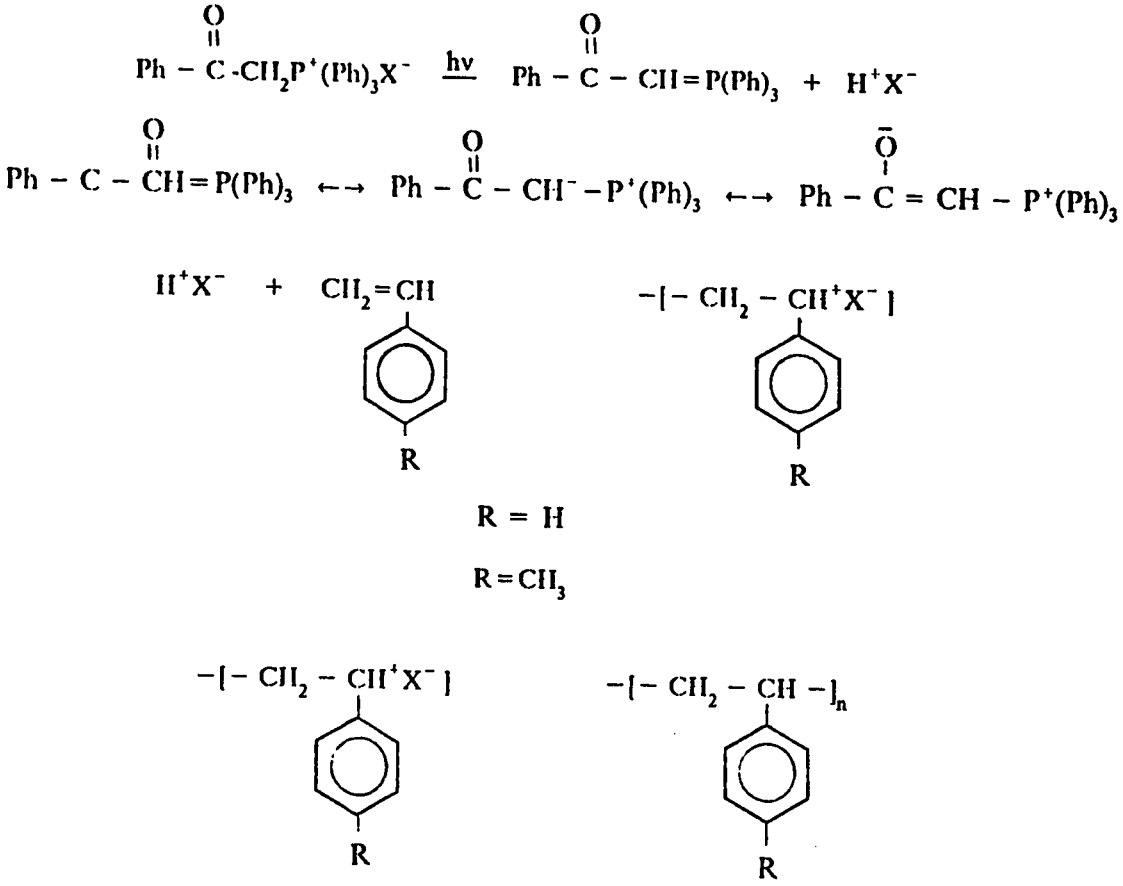
Additive	Irradiation time (Minutes)	% Conversion
Triaryl arsine	480	3.3
Triphenyl phosphine	480	3.3
Tetrabutylammonium hexafluorophosphate	190	5.5
-------	540	7.4

Table (3.12) shows the effect of irradiation of salt alone followed by the addition of styrene on the amount of polymer obtained. These results are similar to those obtained in the p-methylstyrene polymerization and can be explained in the same way.

Table (3.12) **: Effect of irradiation of salt on the rate of polymerisation of Styrene.**

Initiator No.	Irradiation time of salt alone(Minutes)	Total time after mixing (minutes)	% Conversion
27	60	660	zero
2	60	660	90

The suggested mechanism by which photopolymerization of p-methylstyrene and styrene initiated by the phosphonium and arsonium salts is shown in scheme (3.9) :



Scheme (3.9)

3.8 POLYMERIZATION OF METHYLMETHACRYLATE (free radical system) :-

Much attention has recently been paid to the photoinitiated cationic polymerization of epoxides by onium salts for its potential application in industries. However, no works on the free radical photopolymerization by arsonium salts appear to have been reported. In order to examine the possibility of free radical generation in the photolysis of the prepared salts, we examined the photopolymerization of methylmethacrylate in the presence of irradiated salts, since this monomer can not be polymerized by a cationic mechanism. The use of triphenylphosphine as photoinitiator for acrylic monomers has been reported.[24] They were also used as a source of phenyl radicals when heated at 200 °C for crosslinking elastomeric polymers.

A typical example showing the effect of phenacyltriphenyl arsonium salt **27** on the photopolymerization of methylmethacrylate at 25 °C is shown in figure (3.33). Although there is a considerable amount of polymer formed due to the irradiation of monomer alone. It is observed that salt **27** does have an initiation effect. The shape of curve in this figure indicates that in the first two hours salt has no effect on polymerization. Photopolymerization by phenacyltriphenyl arsene (ylid **23**) showed that this ylid acts as an inhibitor since less polymer was obtained compare to irradiation of monomer alone as shown in figure (3.34). These results also showed the amount of polymer obtained depends on the intensity of the irradiation source.

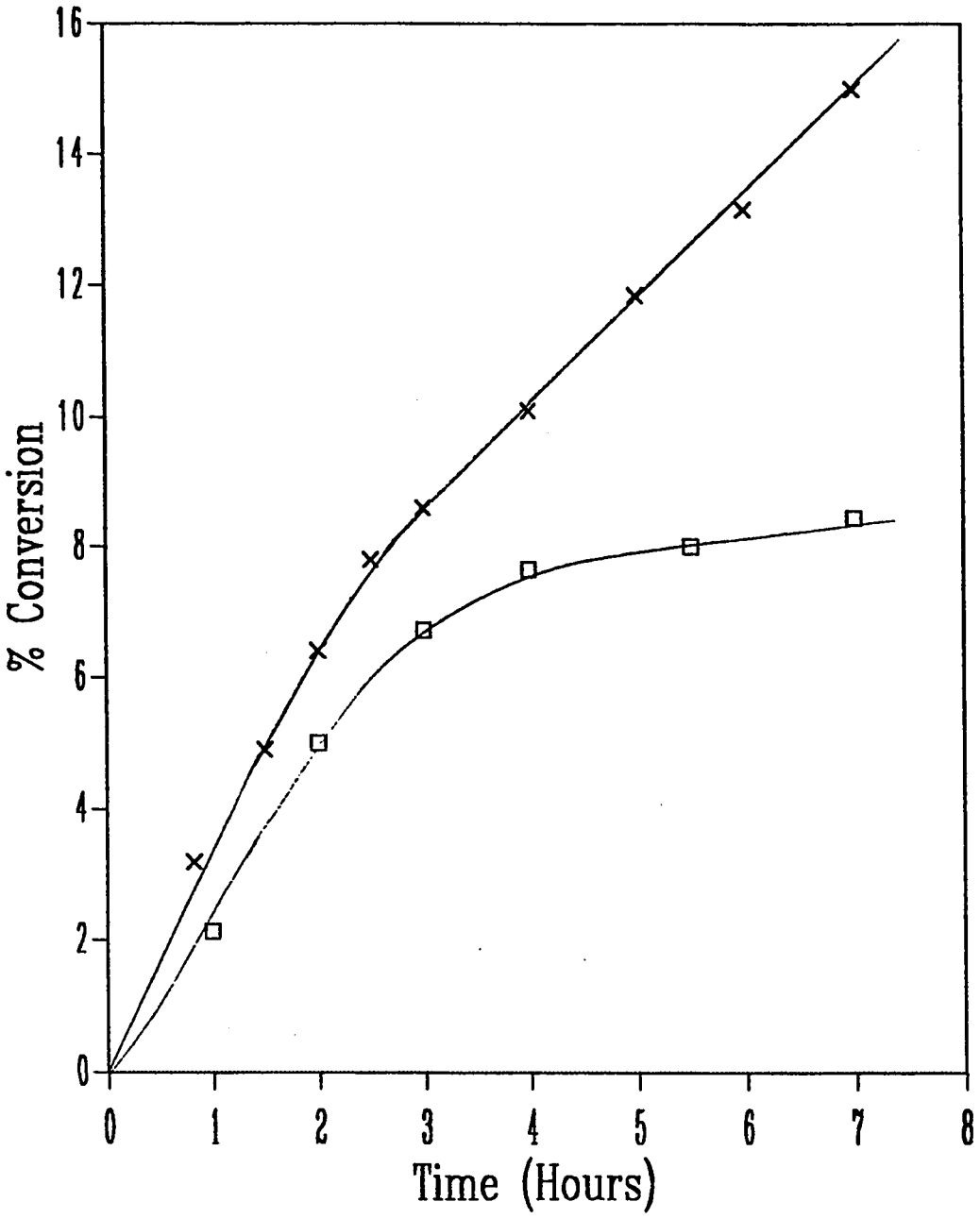


Figure 3.33 : Photopolymerization of methylmethacrylate (□) alone, (×) initiator **27.** (MMA-1,2)

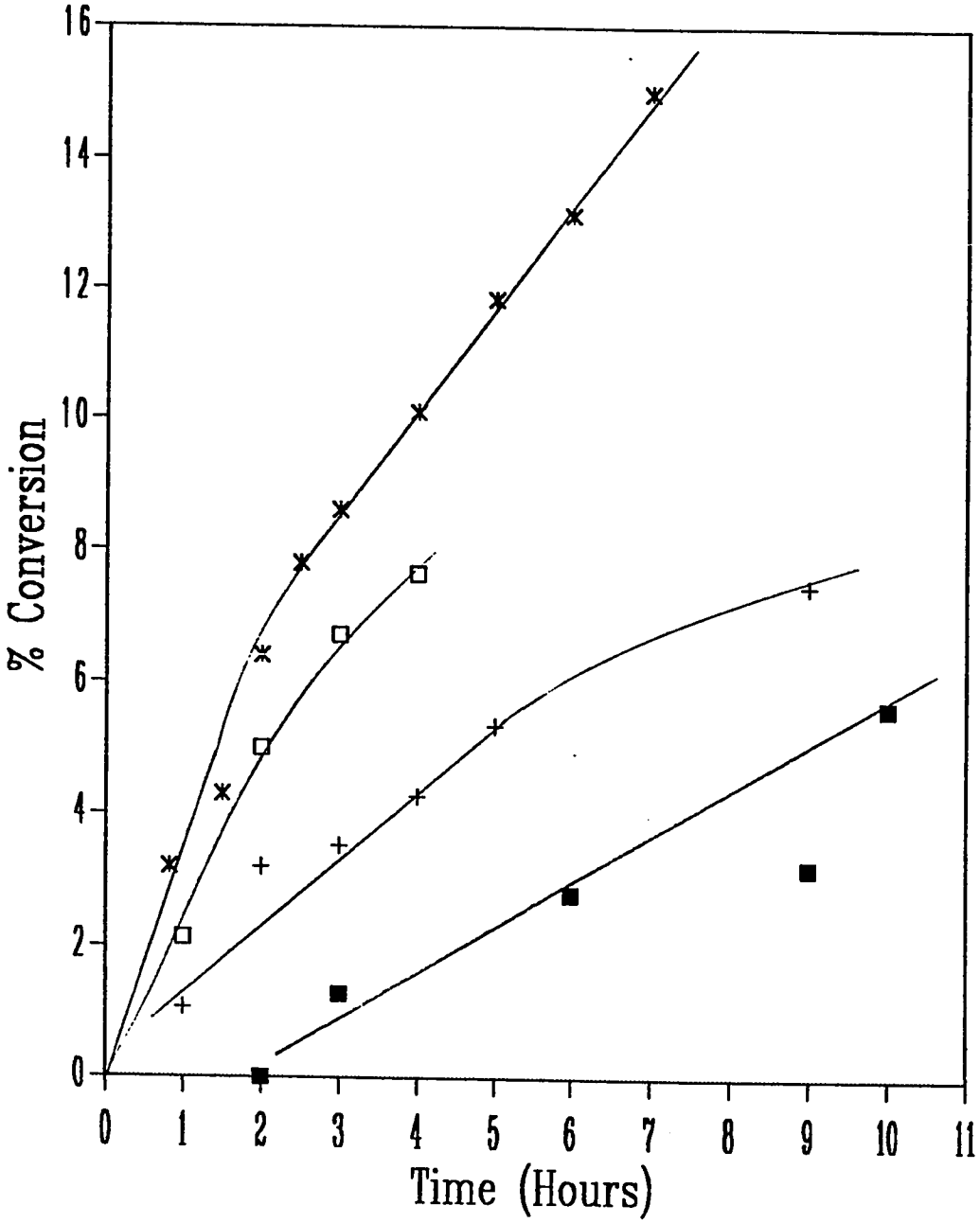


Figure 3.34 : Photopolymerization of methylmethacrylate (□) alone, (✱) initiator **27**, (+) Initiator **27** using 366 nm radiation, (■) ylid **23**. (MMA-1,2,3,4)

CONCLUSIONS

1. The synthesis of various phenacylphosphonium and arsonium salts has been described.

2. Stable phenacylphosphonium and arsonium salts provide a wide range of use as photoinitiators for vinyl and epoxide monomers.

3. Rate of polymerization depends on the salt counter-ion and the intensity of the light source and the conversion to polymer was found to increase with increasing salt concentration.

4. N-methylphenothiazine and pyrene are shown to be effective photosensitizers in the polymerization and their efficiency depends on the monomer type.

5. In case of free radical polymerization of methylmethacrylate it is expected that phenyl radical is the potential initiating species.

6. Polymers obtained here contain phenacylphosphonium or arsonium salt as end group(s). These functionalized polymers may find its application in some ways.

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